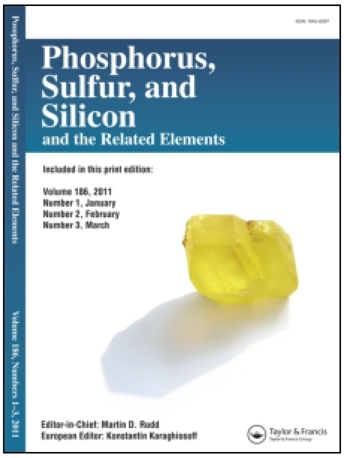

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Szafraniec, Leonard J. , Szafraniec, Linda L. and Aaron, Herbert S.(1987) 'SYNTHESIS, REACTIONS, AND STEREOCHEMICAL CORRELATIONS OF AN OPTICALLY ACTIVE TERVALELENT PHOSPHORUS THIO ESTER', Phosphorus, Sulfur, and Silicon and the Related Elements, 31: 1, 177 — 184

To link to this Article: DOI: 10.1080/03086648708079354

URL: http://dx.doi.org/10.1080/03086648708079354

Phosphorus and Sulfur, 1987, Vol. 31, pp. 177–184
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SYNTHESIS, REACTIONS, AND STEREOCHEMICAL CORRELATIONS OF AN OPTICALLY ACTIVE TERVALENT PHOSPHORUS THIO ESTER

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(Received May 23, 1986)

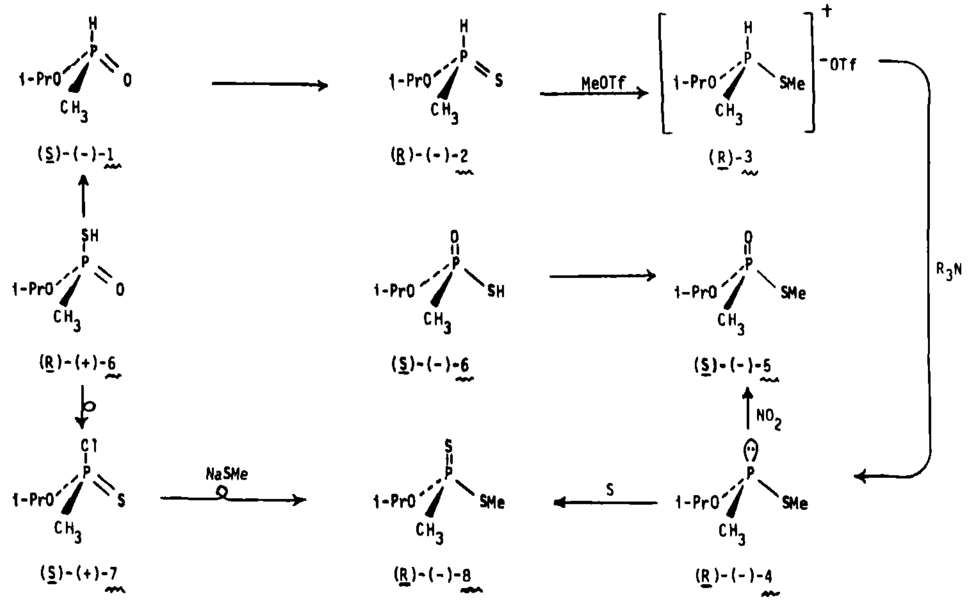
The tetracovalent (*R*)-(−)-isopropyl methylphosphinothionate (**2**) reacts with methyl trifluoromethanesulfonate to form a phosphonium salt (**3**), which yields the tervalent (*R*)-(−)-O-isopropyl S-methyl methylphosphonothioite (**4**) on treatment with triethylamine. However, the reaction is much less stereospecific (~35%) than that of the corresponding P = O analog, **1** (~100%). The (−)-**4** product was characterized and its configuration confirmed by conversion into its corresponding P = O and P = S derivatives, (*S*)-(−)-**5** and (*R*)-(−)-**8**, respectively, which have been related to the known (*S*)-(−) and (*R*)-(+)-O-isopropyl methylphosphonothioic acids (**6**). The triflate product [(−)-**4**] has also been prepared by a relatively simple asymmetric induction reaction that had been reported for a similar compound, and the stereospecificities of the two procedures are compared.

The stereospecific conversion of the tetracovalent (*R*)-(+)-Me(i-PrO)P(O)H into its tervalent (*R*)-(+)-Me(i-PrO)P(OMe) derivative by reaction with methyl triflate has been reported.[1] We now report the results of this reaction with the corresponding thionophosphorus analog for the synthesis of an optically active RP(OR′)(SR″) species. Prior to this study, only one report of an optically active ester of this type was known to us;[2] more recently, three new examples have been published.[3] These were all obtained by an asymmetric induction reaction on a racemic reagent, in which an optically active amine was used to bind an acid byproduct. In these cases, however, the tervalent products were neither isolated nor characterized, but were obtained as reaction intermediates which were directly converted into their corresponding tetracovalent thionate analogs. We have adapted one of these procedures to the present system, to compare to the results obtained by the triflate reaction.

RESULTS

The optically active (*R*)-(−)-isopropyl methylphosphinothionate (**2**) used for this study was synthesized from the reaction of (*S*)-(−)-Me(i-PrO)P(O)H (**1**) with phosphorus pentasulfide (P_4S_{10}).[4] Unexpectedly, the optical purity of the (−)-**2** thus produced was lower than that which had been originally obtained. Upon further investigation, it was determined that the stereospecificity of this reaction varied with the source of the P_4S_{10} that was used. At best, however, the present product was produced in only 35% enantiomorphic excess (ee), compared to the 53% ee that we now believe (see Experimental) had been originally obtained.

In earlier preliminary studies with a racemic model, Me(EtO)P(S)H was found to be much more reactive toward methyl triflate than was its P = O analog. Thus, when the reaction was run at 40°C under the same conditions[1] that had been used for Me(EtO)P(O)H, a sudden exotherm occurred and a multicomponent mixture was obtained, which yielded only 16% of the desired product, MeP(OEt)(SMe). For P = S systems, a better result was obtained by carrying out the reaction at a lower temperature. Thus, as summarized in Scheme 1, when (*R*)-(−)-**2** (13.5% ee) was added to methyl triflate at −10°C, a precipitate of a phosphonium salt (**3**) was formed. This species was not isolated, but was dissolved in a little methylene chloride and added to a solution of triethylamine in benzene at −10°C to give (*R*)-(−)-O-isopropyl S-methyl methylphosphonothioite (**4**), whose chirality was assigned from the fact that it must be formed from (*R*)-(−)-**2** with retention of configuration. This product was obtained as a 10% solution in a solvent mixture of benzene, triethylamine and methylene chloride, 90 mol-% pure by NMR with respect to its organophosphorus content. Since it was observed to racemize on standing in this solution, it was not separated as the neat material, but was converted directly into two stable tetracovalent derivatives, for optical purity determination and stereochemical correlations. Here, a portion of the product was oxidized with nitrogen dioxide[5] to (*S*)-(−)-Me(i-PrO)P(O)SMe (**5**), and a second portion was treated with sulfur to give (*R*)-(−)-Me(i-PrO)P(S)(SMe) (**8**), undoubtedly with retention of the configuration.[6] The chirality and optical purity



SCHEME 1 Stereochemical correlations

of the (*S*)-(−)-**5** product were established by comparison to that which had been obtained from the reaction of methyl iodide with (*S*)-(−)-Me(i-PrO)P(O)SH (**6**),[7] as shown in the Scheme. Thus, the NO_2 oxidation must occur with retention of configuration, the same pathway that has been shown for peracid oxidations.[2,8] The chirality and optical purity of the (*R*)-(−)-**8** were corroborated by comparison to that obtained as (*S*)-(+)-**8** from the reaction of sodium methylmercaptide with (*R*)-(−)-Me(i-PrO)P(S)Cl, a process which is illustrated in the Scheme for the corresponding enantiomorphs, (*S*)-(+)-7 → (*R*)-(−)-**8**. The expected inversion of configuration for this displacement is also corroborated by these results. Finally, to complete the overall Scheme, the known relationship of (*R*)-(+)-**6** to (*S*)-(−)-**1**[9] and to (*S*)-(+)-**7**[10] is also illustrated.[11]

Asymmetric induction reaction. The preceding result was compared to that obtained on treatment of the racemic chiral tervalent phosphorus chloride, $CH_3P(SCH_3)(Cl)$ (**9**), with 2-propanol in the presence of (*R*)-(+)-N,N,α-trimethylbenzylamine. This procedure was adapted from that reported (without experimental detail) for the synthesis of (+)-Et(EtO)P(SEt) in 32% optical purity, determined by examination of its stable thiono (P = S) derivative.[2a]

For our study, the required reagent (**9**) was prepared by a redistribution reaction between $MePCl_2$ and $MeP(SMe)_2$ (**10**). Though not isolated or directly characterized, the (*R*)-(−)-**4** product obtained by our adaptation of this method was found to be 5.1% ee, determined by conversion into its thiono derivative, (*R*)-(−)-**8**. This result is considerably lower than that reported in the literature example cited above.

DISCUSSION

From the above results, the method used for the conversion of the tetracovalent phosphinate **1** into a tervalent phosphonite ester has been shown to be also applicable, but with less stereospecificity, to the corresponding thiono analog **2**. However, a lower temperature had to be used for the P = S system, due to its greater reactivity in the reaction. Even with this modification, the stereospecificity of the reaction was only 35%, compared to the ~100% for the P = O system, apparently due to the greater lability of the thiophosphonium intermediate (**3**). In addition, the isolated thioite product (**4**) appears to be more easily racemized than its tervalent Me(i-PrO)P(OMe) analog, although the two were not actually compared in identical solvent systems.

The optical purities and projected specific rotations of 100% ee **4**, **5**, and **8** and their intermediates are assigned with confidence, based upon the agreement obtained from two independent routes, as summarized in Scheme 1.

The asymmetric induction reaction for the synthesis of optically active thioite esters was much less stereospecific for our compound, compared to the literature example. Nevertheless, this inherently simpler procedure would seem to be the method of choice, if an optically active thioite should be required for stereochemical study.

The mechanism of the asymmetric induction reaction has not been described. The fact that racemic chiral **9** reacts to completion with an *equivalent* of propanol to give an optically active product suggests that a meso intermediate (perhaps a symmetrically solvated phosphorane) may be formed before the stereochemical control of the asymmetric amine takes place, or else the **9** enantiomers must rapidly equilibrate under the reaction conditions.

EXPERIMENTAL

General procedures. Chemical reactions were routinely run using *dried* solvents, and under a dry nitrogen atmosphere. Optical rotations were recorded on a Perkin–Elmer 141 autopolarimeter. The ^{1}H and ^{31}P NMR spectral analyses were performed as described.[1] The δ values refer to ^{31}P chemical shifts, and concentrations are given as weight percent, unless otherwise indicated.

(S)-(−)-Isopropyl methylphosphinate (**1**) was obtained in 54% yield from (*R*)-(+)-O-isopropyl methylphosphonothioic acid (**6**) after correcting for 3.0% ethanol and 11.3% benzene in the distilled product, as determined by ^{31}P and ^{1}H NMR spectral analysis. The specific rotation of the distillate, $[\alpha]_D^{27} - 33.1°$ (*c* 3.94, ethanol), corresponds to $[\alpha]_D^{27} - 38.6°$ (*c* 4.6, ethanol) for the (*S*)-(−)-**1** product (believed to be 100% ee), when corrected for the 14% solvent in the distillate. This specific rotation is about 10% higher than that which one obtains, if the previously reported[1] value is similarly corrected.

(R)-(−)-Isopropyl methylphosphinothionate (**2**). *S*-(−)-**1** (3.6 mmol, from 0.51 g of the 86% sample, above) was added dropwise to a refluxing suspension of 0.25 g (1.12 mmol) of phosphorus pentasulfide (Eastman Kodak Co.) in 15 ml of dry benzene, then refluxed for 8.5 min. After the mixture had cooled, it was shaken with a 5% bicarbonate solution, then with water. The organic layer was dried, filtered and concentrated under reduced pressure to a pale yellow liquid, which was diluted with dry benzene to 1.00 ml (0.913 g) of solution, $\alpha_D - 2.096°$ (1 dcm). By NMR analysis, it contained 15 mol-% of **2** (δ 64.0, $J = 509$ Hz), 83.5 mol-% benzene, and 1.5 mol-% of other phosphorus containing products. This result corresponds to 0.214 g (1.38 mmol, 43% yield) of **2**, $[\alpha]_D^{26} - 9.79°$ (*c* 21.0, benzene), 32% ee by comparison to 100% ee (−) − **2**, $[\alpha]_D - 30.5°$ (benzene).[12]

R-(−)-O-Isopropyl S-methyl methylphosphonothioite (**4**). This reaction was carried out in a three neck flask that had a stopcock drain, and was contained within an attached (glass) cooling bath. To 2.20 g (13.4 mmol) of methyl trifluoromethanesulfonate (methyl triflate, Aldrich Chemical Co.) at −10°C was added dropwise with stirring 0.678 g (4.91 mmol) of (−)-**2**,$[\alpha]_D^{26} - 4.11°$ (*c* 14.6, benzene, 13.5% ee). The temperature was kept at −10°C both during and after the addition. After 30 min, 1 ml of dry methylene chloride was added to dissolve the solid (**3**) that had formed, and the resulting solution was added dropwise via the drain into a stirred and cooled (−10°C) solution of excess triethylamine

(TEA), 3.22 g (31.8 mmol) in 5 ml of dry benzene. The reaction mixture was warmed to room temperature with stirring, and two layers were obtained. The upper layer (6.02 g, 7.10 ml), $[\alpha]_D^{26} - 0.617°$ (1 dcm), was calculated (NMR) to contain 0.58 g (3.8 mmol, 78% yield) of (−)-**4**, and have the following composition: **4** (δ 155.1), 9.6%; benzene, 52.3%; TEA, 25.7%; CH_2Cl_2, 11.1%; six other organophosphorus species, 1.0%. The latter were assigned as $(i\text{-}PrO)_2PMe$(δ 173.8), 0.1%; $(MeS)_2PMe$ (75.5), 0.1%; $(i\text{-}PrO)_2P(O)Me$(27.9), 0.2%; $(i\text{-}PrO)_2P(S)Me$ (100.0), 0.2%; (i-PrO)(H)P(S)Me (63.0), 0.2%; (i-PrO)(MeS)P(O)Me (50.5), 0.2%. From these results, the (−)-**4** product in this layer was calculated to have $[\alpha]_D^{26} - 7.55°$ (*c* 8.17), 4.6% ee, on the basis of the correlations summarized in Scheme 1. This value would have been −56.0° (34% ee), if the (−)-**2** starting material had been 100% ee. Accordingly, 100% ee *R*-(−)-**4** would have $[\alpha]_D^{26} - 164°$ in the solvent mixture described above. A portion of this solution was used to follow its rate of racemization, and the balance was used to prepare (*S*)-(−)-**5** (see below).

Characterization of isopropoxymethylthiomethylphosphonium triflate (**3**). The synthesis of **4** was also run on racemic **2** in an 8 mm NMR tube in CH_2Cl_2, to keep the reaction intermediate in solution for direct NMR examination. Here, at a probe temperature of −20°C, the **3** intermediate (δ 79.3, $J = 607$ Hz) was observed to form to the extent of 10% after 5 min, and 78% after 52 min, accompanied by a corresponding decrease in **2**. When the reaction was then allowed to warm to ambient temperature *without* addition of base, a multicomponent product mixture was observed to form, in which the decomposition of **3** was essentially complete in 1.5 hr.

Rate of racemization of (*R*)-(−)-**4**. A 1.0 ml portion of the 7.10 ml of the upper layer benzene/TEA/CH_2Cl_2 solution of (*R*)-(−)-**4**, above, was monitored at 26°C in a micropolarimeter tube. The sample was observed to racemize at a first order rate ($k = 6.77 \times 10^{-3}\ hr^{-1}$, $\Delta T_{1/2}$ 102 hr) to 62% of its original value after 69 hr. It was then converted into (*R*)-(−)-**8**, as described below.

(*S*)-(−)*O-Isopropyl S-methyl methylphosphonothiolate* (**5**). Dry methylene chloride (5.0 ml) was added to 0.50 g (3.3 mmol) of (−)-**4**, from 5.9 ml of the top layer of the reaction product described above. The resulting solution was cooled in a dry ice-acetone bath, and 1.40 ml of a 10.7% solution of nitrogen dioxide in methylene chloride (0.21 g, 4.6 mmol NO_2) was added dropwise with stirring. The mixture was allowed to warm to room temperature, then concentrated under reduced pressure to give a dark brown liquid, which was distilled twice to give 0.33 g of distillate, bp 34–36°C/0.25 mm, which contained 0.23 g (46% yield) of **5** (δ 51.4) on the basis of the NMR analysis given below. A 300 mg portion of this distillate, diluted to 1.00 ml with benzene, gave 0.928 g of solution, $[\alpha]_D^{26} - 0.918°$. By NMR analysis, it was calculated to have the following composition: **5**, 24.5%; benzene, 67.5%; protonated TEA, 2.3%; TEA oxide, 0.4%; other phosphorus compounds, 5.3%. From these results, the (−)-**5** content was calculated to have $[\alpha]_D^{26} - 4.04°$ (*c* 22.7, benzene), 4.6% ee based upon the reported[7] value of +87.8° (benzene) for 100% ee (+)-**5**. The specific rotation of this (−)-**5** product would have been −29.9° (34% ee), if the (*R*)-(−)-**4** starting material had been prepared from 100% ee (*R*)(−)-**2**.

(R)-(−)-O-Isopropyl S-methyl methylphosphonodithioate (**8**) *from* (*R*)-(−)-**4**. The 1.00 ml solution containing (*R*)-(−)-**4** (0.082 g, 0.54 mmol), which had been used to follow the rate of racemization, was cooled to 2°C, and 0.018 g (0.56 mol) of sulfur was added. A 10°C exotherm was observed. The mixture was allowed to stir at ambient temperature for 2 hr, then filtered, and brought to 1.00 ml with dry benzene. This solution (0.855 g) had the following composition by NMR analysis: **8** (δ 100.2), 7.8%; benzene, 67.5%; TEA, 17.6%; methylene chloride, 4.8%; other phosphorus compounds, 1.1%. The (−)-**8** product in this solution was calculated to have $[\alpha]_D^{26} - 3.18°$ (c 6.67, benzene), which corresponds to 2.96% ee, by comparison to 100% ee (*S*)-(+)-**8**, determined below. The specific rotation would have been −38.0° (35.4% ee), if the (*R*)-(−)-**4** starting material had been prepared from optically pure (*R*)-(−)-**2**, and then directly used for this reaction.

(R)-(−)-O-Isopropyl methylphosphonochloridothionate (**7**) *from* (*S*)-(−)-**6**. To a stirred slurry of 2.70 g (13.0 mmol) of phosphorus pentachloride in 7 ml of dry ether, maintained at −6 to 2°C, was added a solution consisting of 2.00 g (13.0 mmol) of (*S*)-(−)-O-isopropyl methylphosphonothioic acid (**6**), $[\alpha]_D^{28} - 12.40°$, in 5 ml of dry ether. The reaction mixture was stirred for 1 hr at 0°C, filtered, then concentrated on a rotary evaporator under reduced pressure. The residual yellow liquid was distilled twice to give 1.40 g (58.3%) of (*R*)-(−)-**7**, bp 50–52°C/3.5 mm, 95% pure by NMR analysis (δ 94.5), with 5% of an apparent $MeP(S)(OR)_2$ impurity (δ 93.9). This product had $\alpha_D^{26} - 48.5°$ (neat), after correction for its purity, which corresponds to 49.0% ee.[10]

Determination of specific rotation of 100% *ee* (*S*)-(+)-**8**. The 49% ee (*R*)-(−)-**7** above, 1.31 g (7.20 mmol) in 2 ml of benzene, was added with stirring to a suspension of sodium methylmercaptide, from 0.25 g NaH (10 mmol) in 5 ml of methanethiol and 20 ml benzene. The mixture was stirred for 4 hr at ambient temperature then 1.5 hr at 50°C, filtered through Celite, and concentrated under reduced pressure. The residual oil was distilled to give 1.03 g (73.5% yield, corrected) of (*S*)-(+)-**8**, bp 61–63°C/1.0 mm, 94.5% pure by NMR analysis (δ 99.8), with 5.0% of a $MeP(S)(OR)_2$ impurity (δ 93.9). The product had $[\alpha]_D^{26} + 52.8°$ (c 5.15, benzene), corrected for its purity, 49% ee assuming the displacement reaction was completely stereospecific. On this basis, a specific rotation of +107.6° is assigned to 100% ee (*S*)-(+)-**8**.

Dimethyl methylphosphonodithioite (**10**). Methanethiol (21.1 g, 0.438 mol) was condensed into a stirred, cooled (−30°C) solution of 25.6 g (0.218 mol) of methylphosphonous dichloride ($MePCl_2$, available from Strem Chemicals as methyldichlorophosphine) in 250 ml of dry ether. Triethylamine (44.1 g, 0.438 mol) was then added dropwise with stirring and cooling, and the mixture was allowed to warm with stirring to ambient temperature. After standing overnight, the precipitate was filtered and washed with 300 ml of dry ether in a dry bag. The filtrate and washings were combined and concentrated to give 12.2 g of a yellow oil, bp 70–73°C/13 mm, 38% yield based on its NMR analysis: **10** (δ 74.7), 95.3%; **9** (156.0), 4.5%; $MeP(O)(SMe)_2$ (59.3), 0.1%.

S-Methyl methylphosphonochloridothioite (**9**). $MePCl_2$ (12.8 g, 0.109 mol) was added to 12.0 g (0.0815 mol, based on 95% purity) of **10**. The mixture was heated at 90°C for 1.5 hr, then distilled through a 7″ Vigreaux column to give 15.8 g, bp 51–53°C/27 mm, 72% yield based on its NMR analysis: **9**(δ 155.7), 95.1%; $MePCl_2$ (192.1), 2.3%; **10** (74.3), 1.9%; $MeP(O)(SMe)_2$ (59.0), 0.3%; MeP(O)(SMe)Cl (40.7), 0.4%.

Synthesis of (*R*)-(−)-**4** *by an asymmetric induction procedure and conversion to* (*R*)-(−)-**8**. A mixture of 0.560 g (9.33 mmol) of dry 2-propanol and 1.39 g (9.32 mmol) of (*R*)-(+)-N,N,α-trimethylbenzylamine (Aldrich Chemical Co.) was added dropwise with stirring and cooling (−70°C) to a solution of 1.20 g (8.20 mmol, based on 88% purity) of **9** in 25 ml ether. The mixture, which now contained amine hydrochloride precipitate, was stirred for 20 min, allowed to warm to −60°C, and without attempting to isolate the **4** product, was treated with 0.30 g (9.4 mmol) of sulfur. The mixture was allowed to warm to room temperature, stirred for 1 hr, filtered, and concentrated. The residue, in benzene, was refiltered through Celite, then distilled to give 1.06 g, bp 60–61°C/1.0 mm, 53% yield based on its composition, as determined by NMR analysis: **8** (δ 98.4), 86.5%; $(i\text{-}PrO)_2P(S)Me$ (93.9), 6.0%; $MeP(S)(SMe)_2$ (91.2), 5.0%; $MeP(S)Cl_2$ (81.8), 1.9%; $MeP(O)(SMe)_2$ (60.9), 0.1%; (i-PrO)P(O)(SMe)Me (50.6), 0.5%. The (*R*)-(−)-**8** in this product had $[\alpha]_D^{26} - 5.51°$ (*c* 4.33, benzene) after correction for its observed purity, which corresponds to 5.1% ee, by comparison to that of 100% ee (*S*)-(+)-**8**, above. In an attempt to improve on these results, a modified procedure was also tried, in which the (+)-amine and then the 2-propanol were added sequentially to **9** at −74°C. In this case, however, the (*R*)-(−)-(**4**) product isolated as above was only 3.7% ee.

ACKNOWLEDGMENT

We thank Mr. David I. Rossman for samples of the (+) and (−)-**6**.

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11. In Scheme 1, the reagents are designated only for those reactions which are first reported at this time.
12. The previously assigned[9] value of $[\alpha]_D$-24° (benzene) for 100% ee (−)-**2** was based upon its conversion into (+)-Me(i-PrO)P(S)Cl (**7**), which had been erroneously assumed to have $[\alpha]_D$-69.9° (CCl_4) for 100% ee material. While the specific rotation for **7** was reported[9] only for a chloroform solution, values of $[\alpha]_D + 66.0°$ (benzene) and $[\alpha]_D + 77.7°$ (neat, 1 dcm) also had been recorded (L. P. Reiff, unpublished data). However, this sample was apparently only 78.5% ee, because 100% ee **7** has since been tentatively assigned as $[\alpha]_D + 98.9°$ (neat, 1 dcm).[10]