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A New, Stereoselective Interconversion of Phosphinothio- Phosphinoseleno Compounds, Reduction of Phosphinoseleno Derivatives and retro Pishchimuka Rearrangement Based on Methylthio- and Methylselenophosphonium Salts Chemistry

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Abstract: The interconversion of thiono- into seleno compounds was found to proceed with retention of the configuration at phosphorus and the mechanistic course of this process has been proposed. The isomerization reaction of phosphinothiolates into thiono-isomers via the phosphonium salts has been developed and considered as the "retro Pishchimuka" rearrangement.

Key words: interconversion of thiophosphoryl and selenophosphoryl compounds;
methylthio-methylseleno-phosphonium salts;
isomerization of phosphinothiolates into tiono isomers.

INTRODUCTION

Conversion of the phosphoryl group, P=O, into the thiophosphoryl group, P=S and the reverse process is of importance from the synthetic and stereochemical points of view.[1] Sulfurization of the phosphoryl as well as the carbonyl compounds can be simply accomplished using one of a few sulfur "rich" reagents such as phosphorus pentasulfide, boron trisulfide, thiophosphoryl bromide, Lawesson's reagent or its various modifications.[2] Similarly there is a variety of oxidizing agents available for oxidation of thio- or seleno-derivatives.[3] However, the methods for direct P=S⇄P=Se interconversion are practically unknown in the chemical literature.

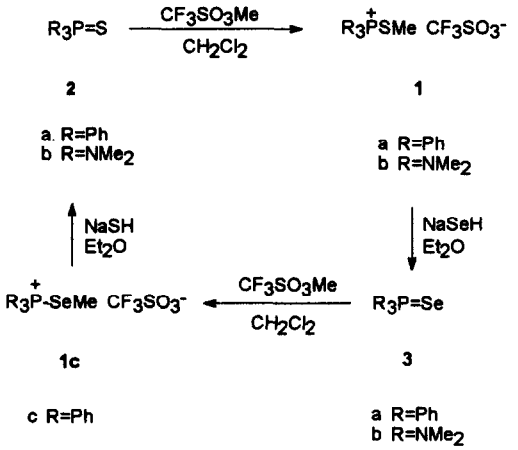
In this paper we would like to report[4] on a new type of the above mentioned interconversion based on the utilization of the phosphonium salts **1** bearing alkylthio- or alkylseleno groups. Moreover, we describe a new, highly stereoselective procedure for the deselenylation of optically active selenophosphoryl compounds via the salts **1** as well as the first example of the isomerization reaction of phosphinothiolates into thiono-isomers which can be considered as the "retro Pishchimuka" rearrangement.

Up to now, the phosphonium salts **1**, although known for long time[5], have been rather rarely used in stereochemical studies. They served only as substrates in the investigation of the mechanism of nucleophilic

substitution at phosphorus.[6] However, an increased interest in chiral alkylthio- and alkylselenophosphonium salts has recently been observed. This is undoubtedly connected with their application as convenient substrates in the stereoselective synthesis of optically active trivalent phosphorus acid esters, amides, tertiary phosphines and chlorophosphines.[7,8]

RESULTS AND DISCUSSIONS

In the preliminary experiments we found that addition of the salt **1a**, prepared by methylation of triphenylphosphine sulfide **2a** with methyl trifluoromethanesulfonate (triflate) in CH_2Cl_2 solution, to a suspension of sodium hydrogen selenide in ether at 0° gives triphenylphosphine selenide **3a** in 59% yield. The same reaction with **1b** proceeds much slower and after six days at room temperature the conversion of **1b** into **3b** was observed in 41% only. On the other hand, the salt **1c** gave upon addition to a suspension of sodium hydrogen sulfide in ether at room temperature triphenylphosphine sulfide **2a** in 59% yield (Scheme 1).

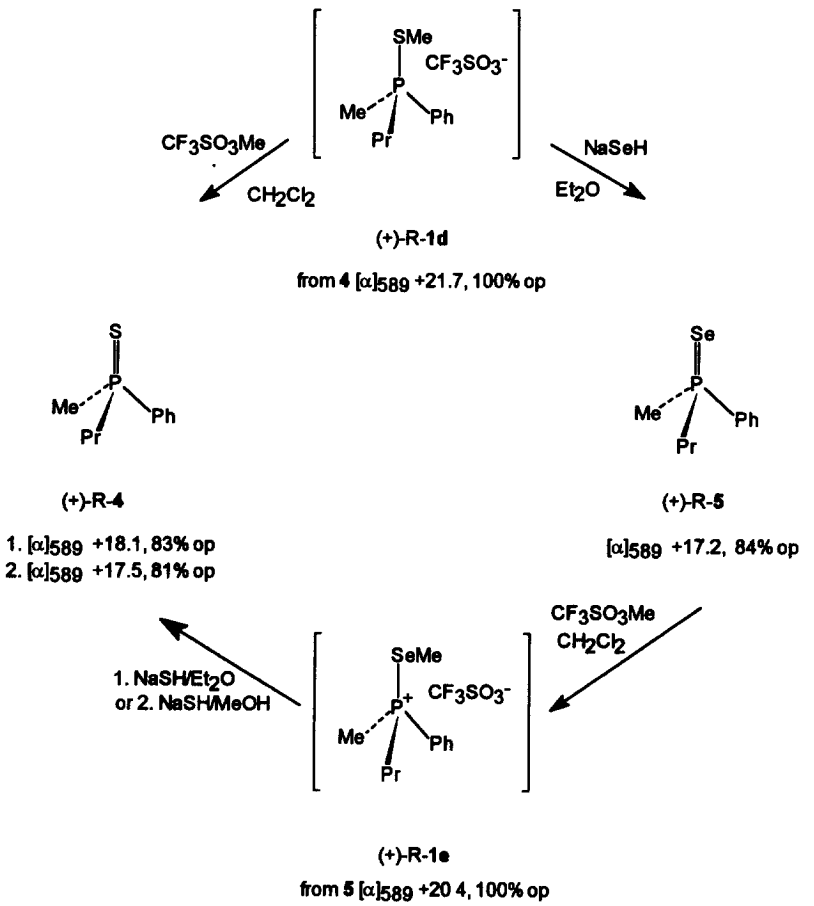


Scheme 1

The course of the latter reaction was monitored by ^{31}P-NMR spectroscopy. The first spectrum was recorded after two hours from mixing both components i.e. **1c** and sodium hydrogen sulfide. In the spectra, in addition to the expected signal of triphenylphosphine sulfide **2a** (δ=42.1 ppm, 57%), three other peaks were observed, which could be ascribed to the following side-products: triphenylphosphine oxide, $Ph_3P{=}O$ (δ=26.3 ppm, 11%); ethyltriphenylphosphonium triflate, $EtPh_3P^+ CF_3SO_3^-$ (δ=21.3 ppm, 17%) and triphenylphosphine Ph_3P (δ=-6.0 ppm, 15%).[9]

The presence of triphenylphosphine in the reaction mixture is the most striking observation. The assumption that triphenylphosphine can be an intermediate in the reaction discussed, prompted us the carry out the experiments with optically active substrates. Thus, the salt (+)-R-**1d**, prepared from the sulfide (+)-R-**4** ($[\alpha]_{589}$=+21.7, 100% op) in the standard way, was added to a suspension of sodium hydrogen selenide in ether at -60°. After the usual work up, the selenide (+)-(R)-**5** ($[\alpha]_{589}$=+17.2, 84%op) was isolated by column chromatography in 41% yield. Similarly, the salt (+)-R-**1e** derived from (+)-R-**5** ($[\alpha]_{589}$=+20.4, 100% op) was added to sodium hydrogen sulfide in ether at -70°. Separation and purification as above gave the sulfide

(+)-R-4 ($[\alpha]_{589}$ = +18.1, 83% op) in 62% yield. Almost the same stereochemical result was observed when the latter reaction was performed in a methanol solution (homogeneous conditions). The experimental results presented above are summarized in Scheme 2.

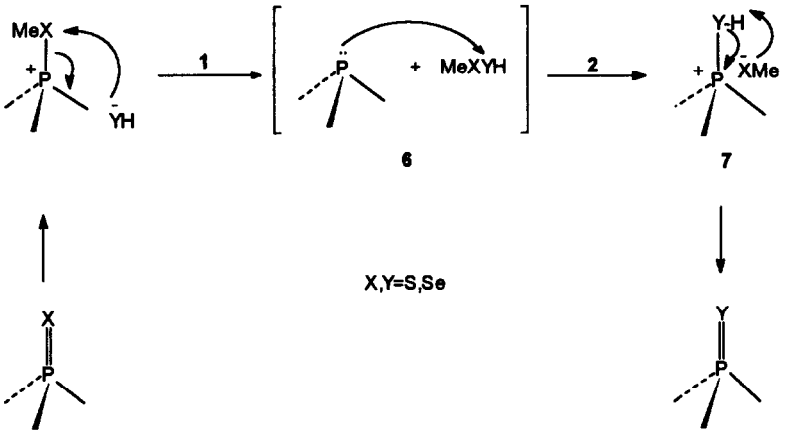


Scheme 2

Since(+)-R-4 and (+)-R-5 are homochiral[5,11], the above stereochemical outcomes allow to draw a conclusion that the interconversion 4 ⇄ 5 proceeds with retention of configuration at phosphorus and with stereoselectivity higher than 90%. Such a stereereochemical course of the P=S ⇄ P=Se transformation in conjuction with the ^{31}P-NMR studies presented above, suggest the following two-step reaction pathway.

The first step of the reaction would consist in the attack of $^-$YH anion on the heteroatom X (S or Se) in 1, which leads to the formation of the tricoordinate phosphorus compound 6 and MeXYH molecule. In the second stage, the P^{III} compound 6 behaves as a nucleophile and attacks the terminal heteroatom Y of MeXYH to give a new phosphonium salt 7, which is transformed to the final product by proton abstraction. Since in every step of the reaction outlined on the Scheme 3 the phosphorus atom preserves its configuration, the overall

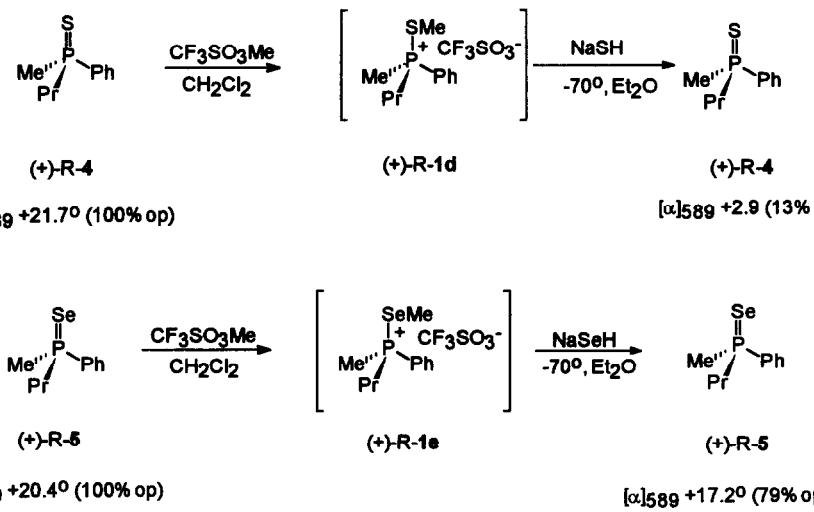
retention of this process is observed.



Scheme 3

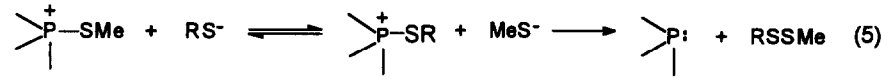
These mechanistic conclusions are in a good agreement with the results of Tsurugi and coworkers[12] who have studied the reaction of achiral trivalent phosphorus compounds with alkyl- or aryl hydrosulfides and who found that the P^{III} reaction component attacks the terminal sulfur atom in hydrodisulfides.

It should be stressed that the selenium atom present in the salt **1** and/or in the reagent plays an important role and exerts a great influence on the stereochemistry of the P=S ⇄ P=Se conversion which can be illustrated by following observations. First of all, treatment of the salt (+)-R-**1d** with sodium hydrogen sulfide reproduces (+)-R-4 sulfide ($[\alpha]_{589}=+2.9°$, 13% op) with predominant retention of configuration accompanied by a substantial racemization. In contrast to that, the analogous reaction between (+)-R-1e and sodium hydrogen selenide is highly stereoselective (~80% op) (Scheme 4).



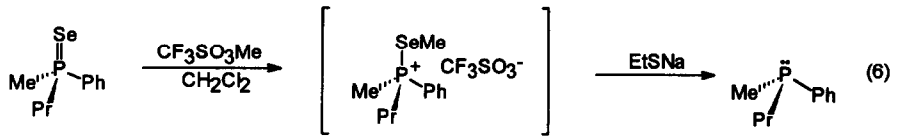
Scheme 4

Since the participation of the mechanism involving an attack of the nucleophile on the sp^3 carbon atom of the SMe and SeMe groups in **1d,e**, seems less likely in the light of the observation that the reactions discussed are chemoselective, the decrease of stereoselectivity in the former reaction can be explained as follows. An anion HS^- may alternatively attack the phosphorus atom in the salt **1d** probably with inversion of configuration at P, releasing the MeS^- anion which evokes the racemization of **1d** by intermolecular ligand exchange. Since only a slight retention of the configuration of **4** is observed as the overall result of the stereochemical process,the latter reaction seems to be pronounced. This assumption is in agreement with our earlier studies on the reaction of mercaptide anions with phosphonium salts of the type **1d**. We have demonstrated[7a] that the RS^- anion attacks the electrophilic phosphorus centre in **1** prior to the departure of the MeS^- anion in the disulfide form.



(+) or (-) (±)

The above equilibrium is most probably responsible for the complete loss of optical activity of methyl(propyl)phenylphosphine **8** (see ref 7a) as well as for racemization of the salt **1d** in Scheme 4. In a sharp contrast to that, the mercaptide anion behaves as a fully stereoselective deselenylation agent towards **1e** giving the phosphine **8** ($[\alpha]_{589}=+18.3$, 96.3% op) with a high degree of optical activity (eq.6).



(+)-R-**5** (+)-R-**1e** (+)-R-**8**

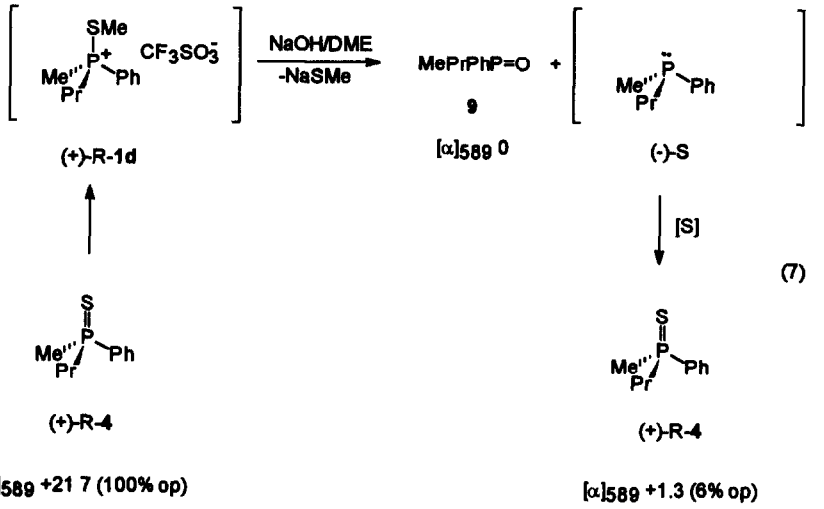
$[\alpha]_{589}$ +18.3 (96 2% op)

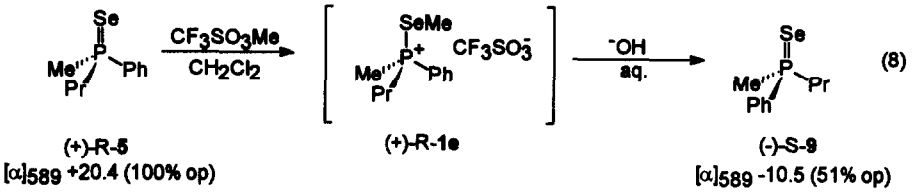
The stereoselective transformation of **5** into **8** via the salt **1e** may be used as a very convenient reduction method of selenophosphoryl compounds. This method is not restricted by the size of the substituents at phosphorus and all transformations are carried out under very mild conditions.

With regard to the behaviour of HS^-, HSe^- anions towards salt **1**, it should be mentioned that a closely related reaction of the alkaline hydrolysis of **1d** affording the corresponding phosphine oxide proceeds with predominant inversion of configuration at phosphorus[13]. However, we found that under heterogeneous conditions the reaction occurs in a different way. Thus, treatment of the (+)-R-**1d** with a powdered sodium hydroxide in a dimethoxyethane (DME) solution of sodium hydroxide affords two products: racemic methyl(propyl)phenylphosphine oxide **9** (67%, ^{31}P-NMR, $\delta=34.1$ ppm) and the phosphine **8** (33%, ^{31}P-NMR, $\delta=-38.4$ ppm) isolated as the corresponding sulfide **5** ($[\alpha]_{589}=+1.3°$, 6% op) ^{31}P-NMR, $\delta=42.5$ ppm). The latter is formed with a slight predominant retention. The presence of a highly racemized **8** in the reaction mixture (eq.7) can be easily explained by assumption that the MeS- anion released and present in the reaction medium causes both, fast racemization of the salt **1d** and competitively acts as a desulfurization reagent.

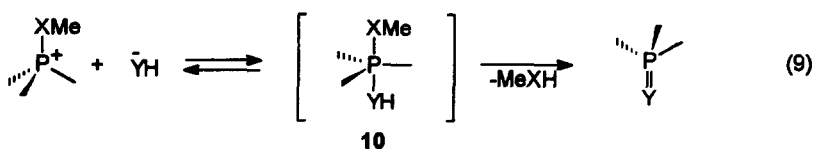
We also found that hydrolysis of (+)-R-**1e** prepared from **5** ($[\alpha]_{589}=+20.4°$, 100% op), carried out in an aqueous solution at 5° to room temperature, gives the oxide (-)-S-**9** with predominant inversion of

configuration (eq.8).

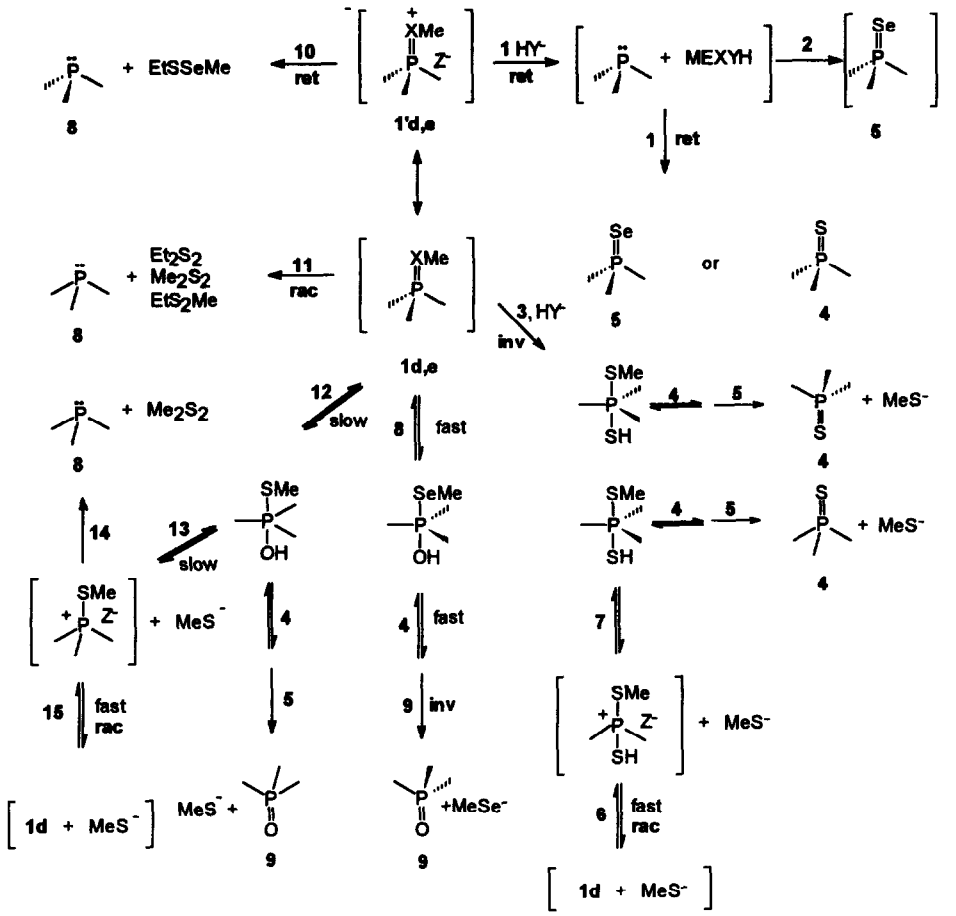




A generally accepted mechanism for the nucleophilic substitution at the phosphorus atom, the consequence of which is the inversion of configuration at the electrophilic centre (as can be seen in the hydrolysis of **1d**), seems to be less likely for the selenolysis or thiolysis of the salts **1** at least for two reasons. The first is that the apical attack of $^-$SH or $^-$SeH anions should form the intermediate **10** (eq. 9) which after decomposition should give a product with inversion. Secondly, the eventual pseudorotation process of **10** should lead to racemization of the substrates, the consequence of which is the racemic product. This is, however, not the case.



The stereochemical results of the reactions of salts **1d,1e** with various nucleophiles hitherto presented are summarized and explained in Scheme 10. The Scheme 10 needs some comments. The products resulting



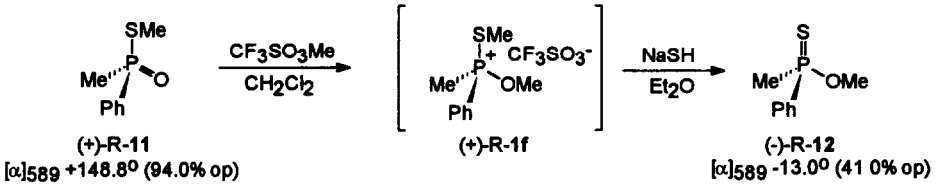
Z=CF_3SO_3
X,Y=S,Se
1=1', X=S, Y=Se or X=Se, Y=S
2.X=Se, Y=Se
3. X=S, Y=S
4. $+H^+$
5. $-MeS^-$
6. 1d ⟶ MeS^-
7. HS^-
8. HO^- aq, X=Se
9 -MeSe
10 EtS^-, X=Se
11, EtS^-, X=S[7a]
12=13 NaOH/DME
14. MeS^-
15. 1d ⟶ MeS^-

Scheme 10

from the preliminary attack of nucleophiles on the phosphorus atom are derived from the mesomeric form **1e,d** (sequences 3→4→5, 6→7→4→5, 8→9, 12→4→5, 11) while those which are formed as a result of a direct attack on the atom X- from the mesomeric form **1'e,d** (sequences 1→1', 1→2 and 10). As can be seen the latter process is observed only when the attacking nucleophile and a leaving group contain various atoms (S or Se) or Se-Se ones. In other cases, the attack of nucleophiles on the phosphorus atom is preferred. However, some examples are known when such an attack can be hampered by introducing bulky substituents at the phosphorus atom or by using highly thiophilic reagents.[7a,b,c]

An important extention of the reaction under discussion is its application for the conversion of optically active phosphinothiolates into the corresponding thiono-isomers. This type of conversion can be defined as the "retro Pishchimuka" rearrangement[14]. It should be stressed that we have succeeded to realize it for the first time.

Thus, treatment of the salt (+)-R-**1f**, (obtained from phosphinothiolate **11** ($[\alpha]_{589}=+148.8°$) with sodium hydrogen sulfide in ether at -70°, provided after a standard work-up and final purification by chromatography phosphinothionate **12** ($[\alpha]_{589}=-13.0$). In a similar way phosphinothiolate (+)-R-**13** ($[\alpha]_D=+141$) was methylated and reacted with sodium hydrogen sulfide to give the phosphinothionate (-)-R-**14** ($[\alpha]_{589}=-25.7$ (eq.11). In this case, however, the most reactive electrophilic centre is undoubtedly the carbon atom of the methoxy group of **1f**, **1g** and therefore the yield of the desired products (**12,14**) is rather low.

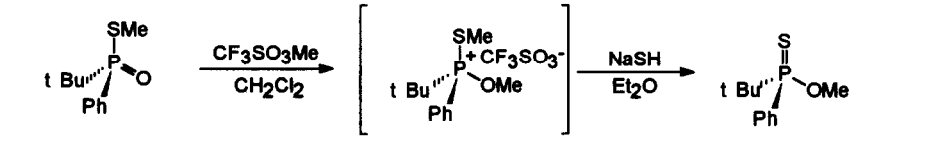


(+)-R-**11**
$[\alpha]_{589}$ +148.8° (94.0% op)

(+)-R-**1f**

(-)-R-**12**
$[\alpha]_{589}$ -13.0° (41 0% op)

(11)



(+)-R-**13**
$[\alpha]_{589}$ +141° (86.6% op)

(+)-R-**1g**

(-)-R-**14**
$[\alpha]_{589}$ -25.7° (59 7% op)

In summary, the results presented in this paper show new applications of the salts **1** for the following reactions: a) stereoselective interconversion of P=S⇄P=Se, b) "retro Pishchimuka" rearrangement, c) stereoselective reduction of selenophosphorus compounds.

Acknowledgement

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EXPERIMENTAL

All boiling and melting points are uncorrected. ^{1}H-NMR and ^{31}P-NMR spectra were measured with a Perkin-Elmer R-12B and a JOEL-JNM FX60 Fourier transform spectrometers at 24.3 MHz with 85% phosphoric acid as external standard, respectively. Optical activity measurements were made with a Perkin-Elmer 241 MC polarimeter. GLC analysis was carried out by using a Varian Aerograph Model 2700 FID gas chromatograph (glass column, silicone OV-101). Solvents were distilled and dried by conventional methods. Methyl triflate supplied by Aldrich Co was used. Sodium hydrogen selenide was obtained by method described by Klaymann and Griffin[15] sodium hydrogen sulfide was prepared by passing dihydrogen sulfide through a solution of sodium ethoxide in ethanol[10]. Optically active methyl-n-propylphenylphosphine sulfide and selenide were obtained by addition of sulfur[5] or selenium[11c] to optically active phosphine, respectively. The latter was synthetized from optically active methyl-n-propylphenylphosphine oxide, prepared according Mislow et al.[16] and deoxygenated with $SiHCl_3$.[17] Optically active S-methyl methylphenylphosphinothiolate was prepared by alkylation[18] of optically active methylphenylphosphinothioic acid which was synthetized as described in literature[19] and resolved by using quinine[20]. The synthesis of t-butylphenylphosphinothioic acid was based on the procedure given by Hoffmann and Schellenbeck[21] its resolution was made with optically active 1-methylbenzylamine[22] and methylation was performed as before[18].

Triphenylphosphineselenide 3a from triphenylphosphine sulfide 2a. To sulfide **2a** (0.29g, 1 mmol) in CH_2Cl_2 (5 mL) triflate (0.16g, 1 mmol) was added at room temperature. The solution of **1a** (^{31}P-NMR, δ=45.9 ppm) was then added dropwise to a suspension of NaSeH (0.2g, 2 mmol) in ether (5 mL) at 0°. After 2h the solid was filtered off and removed of solvents, the crude product was crystalized from benzene/hexane to give triphenylphosphine selenide **3a** 0.2g (59%), mp 181.5-183.5° (lit.[23a], mp. 183-184°), ^{31}P-NMR, δ=34.8 ppm (benzene).

Triphenylphosphine sulfide 2a from triphenylphosphine selenide 3a. To a suspension of NaSH (0.15g, 2.67 mmol) in ether (10 mL) 1c (^{31}P-NMR, δ=35.8 ppm, CH_2Cl_2) obtained from **3a** (0.5g, 1.46 mmol) and triflate (0.24g, 1.46 mmol) in CH_2Cl_2 (5 mL) was added at room temp. The mixture was left overnight and after filtered off a solid the residue was concentrated and chromatographed on column (hexane,benzene, acetane successively were used as eluents) to give Ph_3P=S **2a** (0.25g, 59%) mp 161-3 (lit.[23b], mp. 160.5-161), ^{31}P-NMR, δ=42.2 ppm ($CHCl_3$).

Triphenylphosphine sulfide 2a from triphenyphosphine selenide 3a (^{31}P-NMR assay). To a suspension of NaSH (0.1g, 1.8 mmol) in ether (3 mL) in NMR tube, the salt **1c** (^{31}P-NMR, δ=35.8 ppm, CH_2Cl_2) prepared from **3a** (0.2g, 0.58 mmol) and triflate (0.096g, 0.58 mmol) in CH_2Cl_2 (3 mL) was added at room temp. The mixture was shaked and after 2h was analyzed by ^{31}P-NMR spectroscopy showing the presence of the following peaks: δ=42.1 ppm (57%) Ph_3PS **2a**, δ=-6.0 ppm (15%) Ph_3P; δ=26.3 ppm (11%) Ph_3P=O and δ=21.3 ppm (17%) $EtPh_3P^+$ $CF_3SO_3^-$.

Tris(N,N-dimethyl)amidophosphoroselenate 3b from Tris(N,N-dimethyl)amidophosphorothionate 2b (^{31}P-NMR assay). To a suspension of NaSeH (0.25g, 2,4 mmol) in ether (3 mL) in NMR tube, the salt **1b** (^{31}P-NMR, δ-65.8 ppm, CH_2Cl_2), prepared from 2b (0.3g, 1.5 mmol) and triflate (0.25g, 1.5 mmol) was added at room temp. The mixture was shaked and after 3h analyzed, showing only trace of **3b** (^{31}P-NMR, δ=83.5 ppm). After six days 41% of **3b** and 59% of **1b** was observed.

(+)R-methylpropylphenylphosphine sulfide 4 from (+)R-methylpropylphenylphosphine selenide 5. The salt **1e** prepared from (+)R-**5** (0.3g, 1,2 mmol), [α]589=+20.4, C,2,2, MeOH) and triflate (0.2g, 1.2 mmol in CH_2Cl_2 (6 mL) (^{31}P-NMR, δ=37.5 ppm; $J_{P\text{-}Se}$ 429,7 Hz) was added to a suspension of NaSH (0.08g, 1.5 mmol) in ether (10 mL) at -75°. After warming the mixture to room temp., the solid was filtrated off and the solution was concentrated. The crude product was then chromatographed on column using hexane and then benzene as eluents giving pure (+)-R-**4**, 0.15g, (62%), $[\alpha]_{589}$=+18.1 (c, 1.96, MeOH), ^{31}P-NMR, δ=38.4 (MeOH). GLC showed identity with the autentic sample.

(+)R-methyl-n-propylphenylphosphine selenide 5 from (+)R-methylpropylphenylphosphine sulfide 4. The salt (+)R-**1d** (^{31}P-NMR, δ=52.4 ppm, CH_2Cl_2) from (+)R-**4** (0.3g, 1.5 mmol, $[\alpha]_{589}$=+21.7, MeOH) and triflate (0.24g, 1.5 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a suspension of NaSeH (0.3g, 2.4 mmol) in ether (15 mL) at -60°. The mixture was stirred for 0.5h at -60°, 3h at room temp. and left to stand overnight. The solid was then filtered off, the solution was concentrated and the residue was dissolved in MeOH (5 mL) and filtered. After the solvents evaporation the crude product was chromatographed on column using successively hexane/benzene to give (+)R-**5** 0.15g, (41%) mp. 71.5-74°, $[\alpha]_{589}$=+17.2 (C, 1.18, MeOH) ^{31}P-NMR, δ=25.2 ppm (benzene) (lit.[11c] for pure enantiomer mp. 75-76).

Hydrolysis of (+)R-methyl-n-propylphenylmethylthiophosphonium triflate 1d in heterogeneous conditions. To a suspension of powdered NaOH (5g, 0.12 mmol) in DME (25 mL) the salt **1d** obtained from **4** (0.2g, 0.99 mmol, $[\alpha]_{589}$=+21.7, MeOH) and triflate (0.16g, 0.99 mmol) in CH_2Cl_2 (5 mL) was added at -60°. The mixture was stirred 4h at the same temp. and warmed to room temp. ^{31}P-NMR spectrum of the mixture showed 2 signals: δ=34.1 ppm (PhMePrP=O, 67%) and δ=-38.4 ppm (MePrPhP, 33%). The solution was filtered into a flask with elemental sulfur (0.1g). After concentration the residue was dissolved in MeOH (5 mL), filtered from the excess of sulfur and MeOH was evaporated. The residue was chromatographed by column using successively hexane, benzene and acetane as eluents. Two compounds were obtained: (+)R-**4** (0.05g, $[\alpha]_{589}$=+2.3°, c, 1.46, MeOH; mp. 56-59; ^{31}P-NMR, δ=42.5 ppm, MeOH) and MePrPhP=O **9** (0.09g, $[\alpha]_{589}$=0, c, 1.54, MeOH; ^{31}P-NMR, δ=39.3 ppm. The purity of both compounds were checked by GLC.

Hydrolysis of (+)R-methylpropylphenylmethylselenophosphonium triflate 1e. The salt (+)R-**1e** (^{31}P-NMR, δ=37.5 ppm, CH_2Cl_2) obtained from (+)R-**5** (0.3g, 1.2 mmol), $[\alpha]_{589}$=+20.4, MeOH) and triflate (0.2g, 1.2 mmol) in CH_2Cl_2 (6 mL) was hydrolysed in 10% NaOH (15 mL) at 5°. The mixture was strirred for 0.5h at 5° and 1h at room temp. Then the solution was extracted with $CHCl_3$ (5x10 mL). After drying and evaporation of the solvent the residue was purified by column chromatography using in sequence benzene, acetone as eluents) to give after distillation at 0.1 torr (-)S-**9** (0.12g, 55%, $[\alpha]_{589}$=-10.5; c, 1.74, MeOH) ^{31}P-NMR, δ=42.5 ppm (MeOH).

(+)R-methyl-n-propylphenylphosphine sulfide 4 from (+)R-methyl-n-propylphenylphosphine selenide 5 in homogenous conditions. To a solution of NaSH (0.5g, 8.9 mmol) in MeOH (20 mL) the salt **1c** from (+)R-**5** (0.2g, 0.8 mmol, $[\alpha]_{589}$=+20.4, MeOH) in CH_2Cl_2 (5 mL) and triflate (0.13g, 0.8 mmol) was added dropwise at -40÷-30°. The mixture was then wormed to room temp., stirred 40 min and left to stand overnight. The solvent was evaporated and ether (15 mL) was added. The solution was filtered, concentrated and the residue was chromatographed on a column (using in sequence hexane and benzene as eluents) to give (+)R-**4**, 0.1g (62.5%), mp. 61.5-64°, $[\alpha]_{589}$=+17.5 (MeOH); ^{31}P-NMR, δ=39.4 (MeOH).

(+)R-methyl-n-propylphenylphosphine sulfide 4 from (+)R-salt 1d. The salt (+)R-**1d**, prepared from (+)R-**4** (0.2g, 1 mmol, $[\alpha]_{589}$=+21.7, c, 2.10, MeOH) and triflate (0.16g, 1 mmol) in CH_2Cl_2 (5 mL), (^{31}P-NMR, δ=52.4, CH_2Cl_2) at room temp. was added to a suspension of NaSH (0.11g, 2 mmol) in ether (15 mL) at -70°. The mixture was stirred 5 min and slowly warmed to room temp. After filtered off the solid, the solution was concentrated and the residue was chromatographed by column (hexane and then benzene were used as eluents) giving (+)R-methyl-n-propylphenylphosphine sulfide **4** (0.12g, 60%, $[\alpha]_{589}$=+2.9, c, 0.97, MeOH, mp. 57-59.5°, ^{31}P-NMR, δ=39.4, MeOH).The substance is pure by GLC.

(+)R-methyl-n-propylphenylphosphine selenide 5 from (+)R-salt 1e. To a suspension of NaSeH (1g, 10.3 mmol) in ether (5 mL), a solution of the salt (+)R-**1e**, obtained from (+)R-**5** (0.3g, 1.2 mmol, $[\alpha]_{589}$=+20.4) and triflate (0.2g, 1.2 mmol) in CH_2Cl_2 (5 mL) was added at -60°. After 1h the reaction mixture was warmed to room temp. and left to stand overnight. Then the solvents were evaporated and MeOH (5 mL) was added. The MeOH solution was filtered and concentrated. To the residue hexane (8 mL) was added and the solution was filtered. After evaporation of hexane the pure (+)R-**5** was precipitated as crystal (0.07g, $[\alpha]_{589}$=+17.2, c, 0.72, MeOH), m.p. 70-74° ^{31}P-NMR, δ=25.2 (C_6H_6). The product is pure by GLC.

Transformation of (+)R-S-methyl methylphenylphosphinothiolate 11 into (-)R-O-methyl methylphenyl-

phosphinothionate 12. A mixture of (+)R-**11** (0.46g, 2.47 mmol, $[\alpha]_{589}=+148.8$, MeOH) and triflate (0.4g, 2.47 mmol) was refluxed in CH_2Cl_2 (10 mL) for 15 min. The mixture was then analyzed by ^{31}P-NMR showing two signals: $\delta=96.4$ ppm, (80%), (+)R-**1f**; and $\delta=57.1$ ppm (20%) this unknown compound is probably diphosphonium salt[24]. The mixture was added dropwise to a suspension of NaSH (0.2g, 3.5 mmol) in ether (10 mL) at -70°. After 1h the mixture was warmed to room temp., stirred 2h and a solid material was filtered off. In ^{31}P-NMR spectra three peaks were found: $\delta=89.3$ ppm (30%) MePhP(S)Me 12, $\delta=44.1$ ppm (45%) MePhP(O)SMe **11** and $\delta=47.5$ ppm (25%) (unknown product). After concentration, the residue was chromatographed by column using successively hexane, benzene and acetone as eluents (-)R-**12** was isolated from the hexane-benzene fraction, 0.04g, $[\alpha]_{589}=-13.0$, c, 1.87, benzene. ^{31}P-NMR $\delta=87.7$ ppm (benzene), GLC showed 100% purity.

Transformation of (+)R-methyl-t-butylphenylphosphinothiolate 13 into (-)R-O-methylphenyl-t-butylphosphinothionate 14. To a suspension of NaSH (0.5g, 8.9 mmol) in ether (10 mL) the salt **1f** (^{31}P-NMR, $\delta=110.4$, CH_2Cl_2 with some byproduct $\delta=87.7$ ppm23) prepared from (+)R-**13** (1g, 3.96 mmol, $[\alpha]_{589}=+141$. benzene) and triflate (0.65g, 3.96 mmol) in CH_2Cl_2 (10 mL) was added at room temp. The mixtures was stirred 2h and analyzed by ^{31}P-NMR spectroscopy showing three signals: $\delta=106.0$ ppm, (Pht-BuP(S)OMe, **14**, 12%), $\delta=67.5$ ppm (Pht-BuP(O)SMe, **13**, 80%) and $\delta=51.9$ ppm, (unknown compounds, 8%). The mixture was filltered off, the solvents were evaporated and the residue was chromatographed with preparative TLC (Kiesel gel, Merck, benzene: acetone: n-propanol, 2:1:1 as a mobile phase) to give after isolation (-)R-O-methyl t-butylphenylphosphinothionate **14** (0.05g, $[\alpha]_{589}=-25.7$, C, 2.73, MeOH), ^{31}P-NMR, $\delta=106.5$ (MeOH), ^{1}H-NMR, $\delta=1.4$ ppm (9H, d, $J_{P\text{-}O\text{-}C\text{-}H}=13.0$ Hz) t-Bu, $\delta=3.5$ ppm (3H, d, $J_{P\text{-}O\text{-}C\text{-}H}=10.9$ Hz) MeO, $\delta=7.2$-8 ppm (5H, m) Ph and (+)S-methyl t-butylphenylphosphinothiolate **13**, (0.3g, $[\alpha]_{589}=+88.7$, C, 0.94, MeOH); ^{31}P-NMR, $\delta=66.5$ ppm, (MeOH). The purity and additional identity was checked by GLC.

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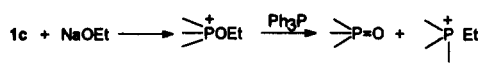
9. Presence of ethyltriphenylphosphonium triflate and triphenylphosphine oxide as side-products in the reaction mixture can be explained as the result of the reaction of **1c** with sodium ethoxide which probably exists as an admixture in sodium hydrogen sulfide.



The procedure[10] for the preparation of sodium hydrogen sulfide consists in passing dihydrogen sulfide through a solution of sodium ethoxide in ethanol leading to the following equilibrium.

Isolation of sodium hydrogen sulfide is then followed by precipitation of the product with ether and co-precipitation of some amounts of sodium ethoxide is also possible.

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24. It was found that alkylation of the ester **11** with a half molar ratio of triflate at room temperature after long time reaction (some month) gave a viscosous substance. On the basis of its elemental analysis, alkaline hydrolysis and spectral data: [^{31}P-NMR, δ=87.7 ppm (CH_2Cl_2); ^{1}H-NMR, δ=1.82 ppm, d, $J_{P\text{-}C\text{-}C\text{-}H}$=18.7 Hz, t-Bu (9H); δ=2.81 ppm, d, $J_{P\text{-}S\text{-}C\text{-}H}$=12.0 Hz, Sme (3H) and δ=8.33 ppm, m, (5H), Ph] a structure of diphosphonium salt[25], Ph(t-Bu)P(SMe)-O-P(SMe)Ph(t-Bu)$_2$$CF_3SO_3^-$, may be ascribed as the result of the reaction of **11** with **1f.**
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