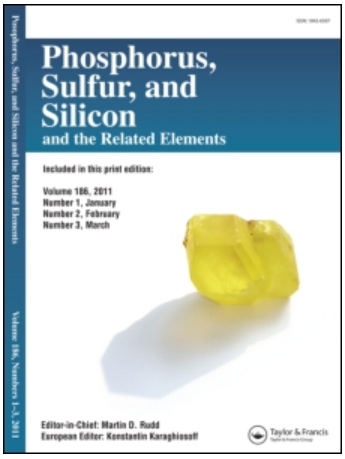

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STEREOSPECIFIC INTERCONVERSION OF THIO- AND SELENOPHOSPHORYL COMPOUNDS

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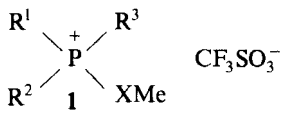
The conversion of chiral methyl-*n*-propylphenylphosphine sulphide into the corresponding selenide and the reverse reaction are easily accomplished by treatment of the corresponding methylthio- and methylselenophosphonium salts with sodium hydrogen selenide and sodium hydrogen sulphide, respectively. Both reactions occur with retention of configuration at phosphorus and high stereospecificity.

Although chiral phosphonium salts bearing an alkylthio group on phosphorus are known a long time,[1] their use in stereochemical studies was rather sparse and restricted to the investigation of the mechanism of nucleophilic displacement at phosphorus.[2] The renewed interest in chiral alkylthio- and alkylselenophosphonium salts is undoubtedly caused by the fact that they were found to be convenient starting materials in the stereospecific synthesis of optically active trivalent phosphorus acid esters and tertiary phosphines.[3,4] In this paper we would like to report a new type of the stereospecific $\rangle P{=}S \rightleftarrows \rangle P{=}Se$ interconversion based on the reaction between chiral phosphonium salts **1** and sodium hydrogen sulphide and sodium hydrogen selenide.

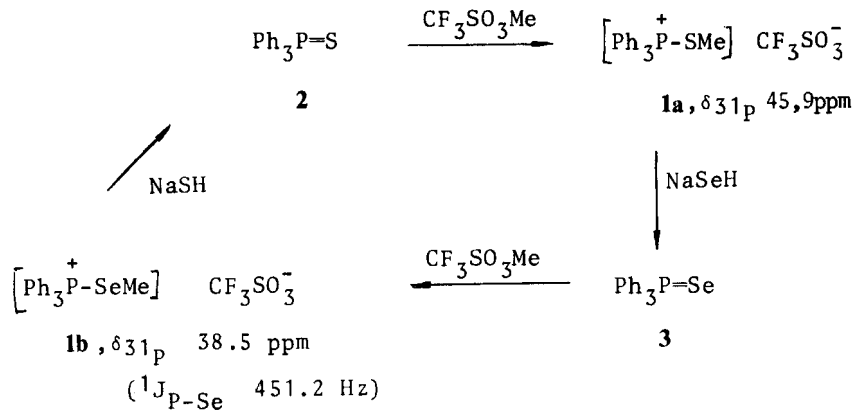


1

a, $R^1 = R^2 = R^3 = Ph$, X = S
b, $R^1 = R^2 = R^3 = Ph$, X = Se
c, $R^1 = Me$, $R^2 = n\text{-Pr}$, $R^3 = Ph$, X = S
d, $R^1 = Me$, $R^2 = n\text{-Pr}$, $R^3 = Ph$, X = Se

Preliminary experiments with triphenylphosphine sulphide (**2**) and triphenylphosphine selenide (**3**) demonstrated that their interconversion may be easily accomplished *via* the corresponding phosphonium salts **1a** and **1b** (Scheme 1). Thus, triphenylphosphine sulphide (**2**) was treated with methyl trifluoromethane-sulphonate in CH_2Cl_2 solution at room temperature to give the salt **1a** which, in turn, was added to a suspension of NaSeH in ether at 0°. After two hours the reaction mixture was worked up affording triphenylphosphine selenide (**3**) in 59% yield. On the other hand, the salt **1b** obtained from triphenylphosphine selenide (**3**) and methyl trifluoromethanesulphonate gave on addition to a suspension of NaSH in ether triphenylphosphine sulphide (**2**) in 57% yield.

The progress of the latter reaction was monitored by the ^{31}P NMR spectra which revealed that triphenylphosphine is the reaction intermediate. It was also found that



SCHEME 1

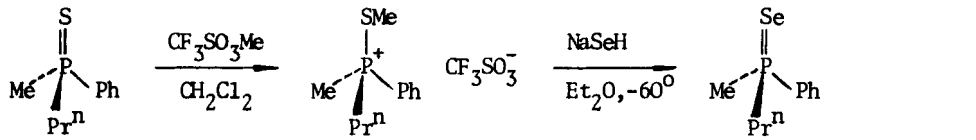
triphenylphosphine oxide, Ph_3PO ($\delta_{^{31}P}$, 26.3 ppm), and methyltriphenylphosphonium trifluoromethanesulphonate, $Ph_3\overset{+}{P}Me\ CF_3SO_3^-$ ($\delta_{^{31}P}$, 21.3 ppm), are formed as side-products.[5]

In order to gain better insight into the mechanism of the $\rangle P{=}S \rightleftharpoons \rangle P{=}Se$ conversion the experiments with optically active (+)-(R)-methyl-*n*-propylphenylphosphine sulphide (**4**)[1] and the corresponding (+)-(R)-selenide (**5**)[6] were carried out. In this case, however, slightly different experimental conditions were applied. The salt (+)-(R)-**1c**, prepared from (+)-(R)-**4** in a standard way in CH_2Cl_2 solution, was added dropwise to a suspension of NaSeH in ether at $-60°$. Then, the reaction mixture was slowly warmed to room temperature and left to stand overnight. After the usual work-up (+)-(R)-selenide (**5**) was isolated by column chromatography (silica gel; hexane–benzene) in 41% yield. Similarly, the salt (+)-(R)-**1d** obtained from (+)-(R)-**5** was added to a suspension of NaSH in ether at $-70°$. After a short time the reaction mixture was warmed to room temperature and worked up. After column chromatography (+)-(R)-sulphide (**4**) was obtained in 62% yield.[7] The experiments discussed above are summarized in Scheme 2.

Since (+)-(R)-**4** and (+)-(R)-**5** are homochiral, it is evident that the conversion of (+)-(R)-**1c** into (+)-(R)-**5** and (+)-(R)-**1d** into (+)-(R)-**4** shown above occur with retention of configuration at phosphorus. The stereospecificity of both reactions is higher than 90%.

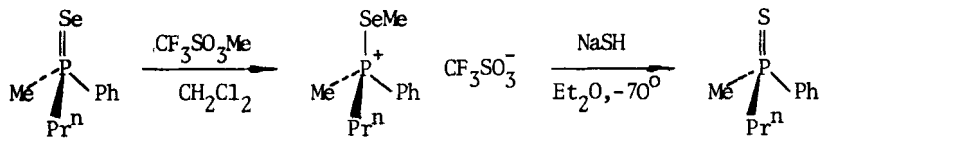
Such a stereochemical result in combination with the ^{31}P NMR detection of triphenylphosphine as an intermediate in the reaction between **1b** and NaSH strongly suggests the following course for the reaction of phosphonium salts **1** with the HS^- and HSe^- anions (Scheme 3).

The first step of the reaction involves the nucleophilic attack of the HY^- anion on the heteroatom X in **1** leading to the formation of phosphine **6** with retention of configuration and the MeXYH molecule. In the second stage phosphine **6** behaves as a nucleophile and reacts with the terminal heteroatom Y of MeXYH to give phosphonium salt **7**.[8] The latter is stabilized to the final reaction product by proton removal. Since the second reaction step is undoubtedly connected with retention of



(+)-(R)-**4** (+)-(R)-**1c** (+)-(R)-**5**

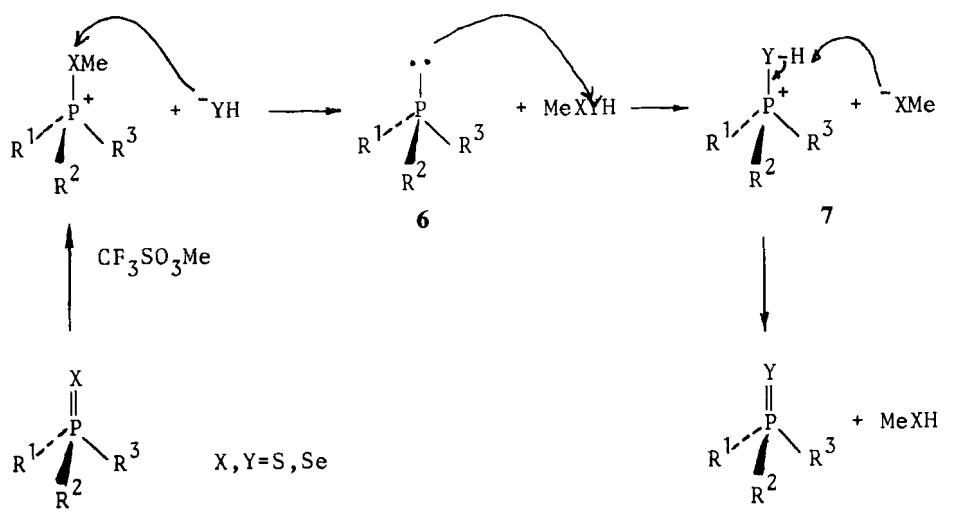
$[\alpha]_{589}$+21.7° (100%e.e.)† $[\alpha]_{589}$+30.8° $[\alpha]_{589}$+17.2° (84%e.e.)



(+)-(R)-**5** (+)-(R)-**1d** (+)-(R)-**4**

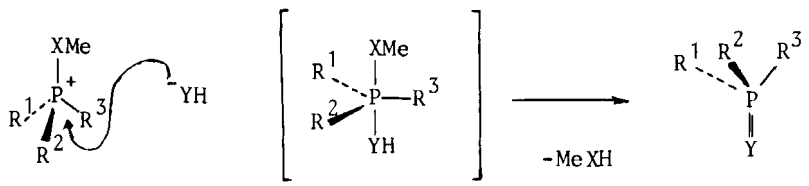
$[\alpha]_{589}$+20.4° (100%e.e.) $[\alpha]_{589}$+31.8° $[\alpha]_{589}$+18.1° (83%e.e.)

SCHEME 2



SCHEME 3

†Optical rotation values of **4** and **5** refer to methanol solution while those of **1c** and **1d** to methylene chloride solution.



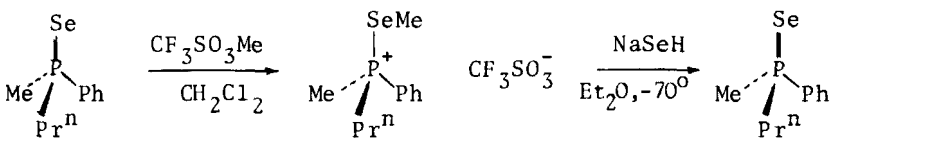
1 **8**

SCHEME 4

configuration at phosphorus, the overall stereochemistry of this process is retention at phosphorus.

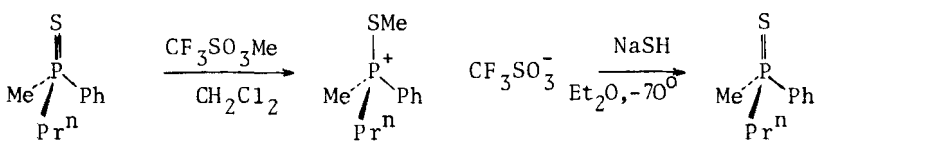
An alternative mechanism involving the nucleophilic attack of the HY^- anion at phosphorus in **1** seems to be less probable for two reasons. The first is that the apical attack of HY^- should result in the formation of the intermediate phosphorane **8** which should decompose to the final reaction product with inversion of configuration at phosphorus as shown in Scheme 4.

In this context it should be noted that the closely related reaction of the alkaline hydrolysis of **1** (X=S) leading to phosphine oxide proceeds with predominant inversion of configuration at phosphorus.[1] Secondly, the eventual pseudorotations of **8** should give the starting material as well as the final reaction product highly or completely racemized. This is, however, not the case.



(+)-(R)-**5** (+)-(R)-**1d** (+)-(R)-**5**

$[\alpha]_{589}$+20.7° (100%e.e)† $[\alpha]_{589}$+27.4° $[\alpha]_{589}$+17.2° (79%e.e)



(+)-(R)-**4** (+)-(R)-**1c** (+)-(R)-**4**

$[\alpha]_{589}$+21.7° (100%e.e) $[\alpha]_{589}$ +30.8° $[\alpha]_{589}$+2.9° (13%e.e)

SCHEME 5

†Optical rotation values of **4** and **5** refer to methanol solution while those of **1c** and **1d** to methylene chloride solution.

Finally, it is interesting to note that the reaction between (+)-(R)-**1d** and NaSeH leading to (+)-(R)-**5** is highly stereospecific in contrast to the analogous reaction between (+)-(R)-**1c** and NaSH which gave highly racemized phosphine sulphide (+)-(R)-**4** (see Scheme 5).

The results presented in Scheme 2 and 4 strongly suggest that the presence of selenium is quite important from the point of view of the attack of thiophilic reagents at sulphur and selenium and not at phosphorus in phosphonium salts **1**. This point is under current study in this laboratory.

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4. L. Horner, *Pure and Appl. Chem.*, **52**, 843 (1980).
5. In a typical experiment the reaction of **1b** with NaSH afforded triphenylphosphine sulphide (**2**), triphenylphosphine oxide, methyltriphenylphosphonium trifluoromethanesulphonate and triphenylphosphine in 57, 11, 17 and 15% yield, respectively. An explanation for the formation of by-products will be given in a full paper.
6. W. J. Stec, A. Okruszek and J. Michalski, *Angew. Chem.*, **83**, 494 (1971).
7. The reaction of (+)-(R)-**1d**, $[\alpha]_{589}$ + 31.4°, with NaSH in methanol, e.g. under homogeneous conditions, gave (+)-(R)-sulphide (**4**) in 64% yield having $[\alpha]_{589}$ + 17.5° (80% e.e.).
8. For a similar reaction between achiral trivalent phosphorus compounds and alkyl or aryl hydrodisulphides see: J. Tsurugi, T. Nakabayashi and T. Ishihara, *J. Org. Chem.*, **30**, 2707 (1965); T. Nakabayashi, S. Kawamura, T. Kitao and J. Tsurugi, *J. Org. Chem.*, **31**, 861 (1966); T. Nakabayashi, J. Tsurugi, S. Kawamura, T. Kitao, M. Ui and M. Nose, *J. Org. Chem.*, **31**, 4174 (1966).