Pergamon

Tetrahedron 54 (1998) 9731–9746

TETRAHEDRON

P-Chiral Thioxophosphoranesulfenyl Chlorides RR'P(S)SCl. A Unique Stereochemical Probe to Study Nucleophilic Displacement at a Dicoordinate Sulfur Center

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Received 26 February 1998; revised 8 May 1998; accepted 29 May 1998

Dedicated to Professor A R Katritzky on the occasion of his 70th birthday

Abstract: A stereospecific synthesis of P-chiral sulfenyl chlorides **6a,b** has been developed from P-chiral sulfenylamide **9a,b,c** by a novel procedure employing $2Me_3SiCl + 2EtOH$ as the reagent of choice. The sulfenylamides **9a,b,c** were prepared either by stereospecific reaction of the P-chiral hydrogen phosphinothioate **8a** with aminosulfenyl halides or separation of a mixture of diastereomeric **9a,b,c** by crystallisation. P-Chiral chlorides **6a,b** were allowed to react with secondary amines such as morpholine or dicyclohexyl amine. All these displacement reactions proceed with almost complete stereochemical integrity at the phosphorus atom. These observations support a synchronous mechanism of bond breaking and bond formation during nucleophilic displacement at the dicoordinate sulfur atom. The same can be said about the reaction of sulfenamides **9a,b,c** with hydrogen chloride.

Derivatives of sulfenic acids of general formula RS-X **1** represent a wide range of structures which are important in heteroatom chemistry. Representative groups R cover alkyl, aryl, acetyl, amino, phosphoryl and thiophosphoryl ligands. The leaving group X may include groups like NR_2, OR, SCN, halogens and CN. We focused our attention on molecules of the type **1** where R represents phosphoryl RR"P(O)- and thiophosphoryl RR'P(S)- groups. The leaving group X includes halogens, NR_2, OR, SR and CN. Many of these structures are readily available, relatively stable, useful as reagents and models for mechanistic studies.[1,2]

Disulfides of the formula $[RR'P(O)S]_2$ **2** which contain two strongly electronegative phosphoryl groups attached to the disulfide core have been recognized as pseudohalogen

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0040-4020/98/$ - see front matter
PII: S0040-4020(98)00529-8

species.[3] Both structure and properties of these compounds **2** resemble the well-known thiocyanogen $(SCN)_2$. Therefore compounds RR'P(O)S-X (X=Br,Cl) **3** can be classified as pseudohalogenohalogens. When R ≠ R', compounds **2** and **3** have a P center of chirality and can exist as enantiomers or diastereoizomers, which are available from corresponding chiral phosphorus monothioacids.[4]

$$RR'P(S)O^{-} \xrightarrow{Me_3SiX} RR'P(S)OSiMe_3 \xrightarrow{SO_2Cl_2} RR'P(O)SCl \quad \mathbf{3}$$

Phosphorus dithioacids RR'P(S)SH **4** are achiral, and synthesis of P-chiral systems $[RR'P(S)S]_2$ **5** and RR'P(S)S-X (X=Br,Cl) **6** requires different strategies to those described for compounds **3** and **5**. This paper describes the efficient synthesis of the P-chiral systems **6** (X=Cl).

Reactions of compounds **3** and **6** with the majority of nucleophiles are similar to those of simple alkane and arenesulfenyl halides.[5] We assumed that P-chiral thioxophosphorane-sulfenyl chlorides RR'P(S)S-Cl **6** (X=Cl) would provide models to study mechanistic aspects of nucleophilic displacement reactions at the dicoordinate sulfur atom. In these models stereochemical integrity at the P-chiral center is indicative for intermediates that are involved in the displacement of ligand X at the dicoordinate sulfur center. The achiral nature of dicoordinate sulfur in **1** precludes any direct investigation of stereochemical changes of nucleophilic displacement in this class of compounds. The recent comprehensive review by Okuyama[6] represents the state of the art in the field of nucleophilic substitution at dicoordinate sulfur.

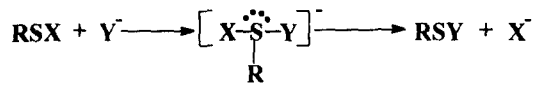
One can postulate three types of process involved in nucleophilic displacement at dicoordinate sulfur. The first involves the sulfenium ion as an intermediate (S_N1 type):

$$RSX \xrightarrow{slow} RS^{+} + X^{-} \xrightarrow{Y^{-}} RSY + X^{-}$$

A second process of the S_N2 type takes place with concerted bond formation and cleavage.

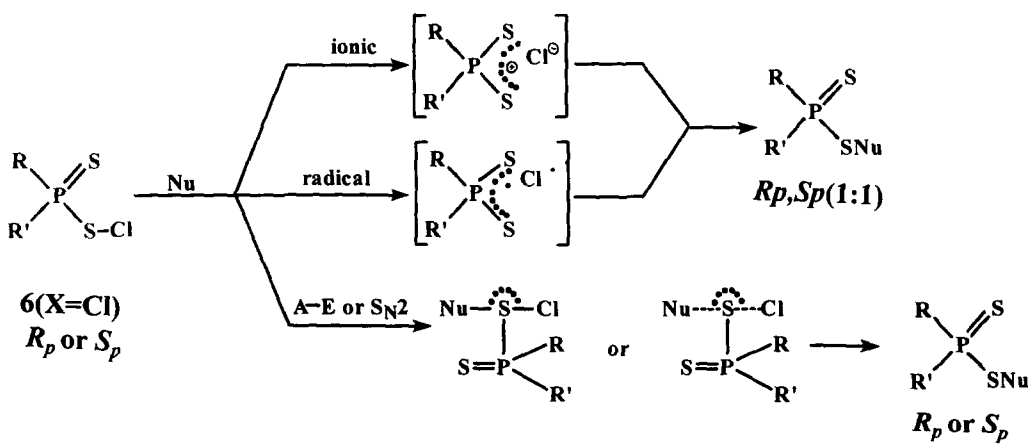
$$RSX + Y^{-} \longrightarrow \left[Y \cdots \underset{R}{S} \cdots X \right]^{-} \longrightarrow RSY + X^{-}$$

A third mechanism in which a discrete intermediate of some stability can exist is an addition-elimination (A-E).



Most of the kinetic results obtained to date allow no clear-cut decision about whether the bimolecular mechanism is stepwise (A-E mechanism) or synchronous (S_N2-type mechanism). In the intramolecular transestrification of a sulfenate ester, a hypervalent intermediate was observed by spectroscopy and this pointed to a stepwise A-E mechanism. Many kinetic results are concerned with the effect of substituents on reaction rate, and do not allow differentiation between A-E and S_N2 mechanisms. Both mechanisms should proceed through a similar transition state. The best way to demonstrate an the A-E mechanism, if the hypervalent intermediate is not detectable spectroscopically, is by systematic variation of the substrate structure, nucleophiles and reaction conditions. Nucleophilic substitution at dicoordinate sulfur generally entails a trigonal bipyramidal intermediate (or transition state) in which the entering and leaving groups occupy the two apical positions. The general conclusion from kinetic studies is that an S_N1 type mechanism is less likely. The possibility of an ion-pair intermediate could not, however, be excluded in the reaction of sulfenyl chlorides with amines.[5]

We decided to use P-chiral thioxophosphoranesulfenyl chlorides RR'P(S)S-Cl **6** (X=Cl) as a stereochemical probe for displacement reactions occurring at dicoordinate sulfur. We anticipated that only those processes in which bond breaking and bond formation proceed in dissociative manner, either ionic or radical, would result in loss of stereochemical integrity at the chiral phosphorus center.

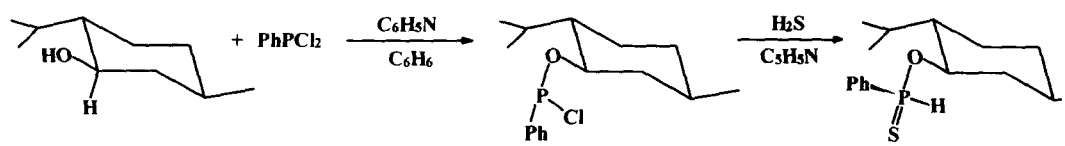


On the other hand, synchronous processes of bond breaking and formation should lead to products with retained stereochemical integrity at the chiral phosphorus center. Such a result should be observed for A-E and S_N2 mechanisms. In order to see whether this challenging assumption was true, we first developed a convenient synthesis of diastereomeric P-chiral thioxophosphoranesulfenyl chlorides of the type **6** (X=Cl) in which the l-menthoxy group serves as the auxiliary source of chirality. Then we looked at the reaction of the diastereomeric P-chiral sulfenyl chlorides **6** (X=Cl) with secondary amines.

Synthesis of Diastereoisomeric Thioxophosphoranesulfenamides.

Our plan was to synthesize the P-chiral diastereoisomeric thioxophosphoranesulfenyl chlorides RR'P(S)S-Cl **6** (X=Cl) from the corresponding thioxophosphoranesulfenamides RR'P(S)-SNR"$_2$ **9**. We took advantage of the high stability of these sulfenamides and their tendency to crystallize easily. The first step was to synthesize compounds of the general formula RR'P(S)H **8** and then to convert them by reaction with aminosulfenyl halides into the thioxophosphoranesulfenamides **9**.

The hydrogen *O-l*-(-)-menthylphenylphosphinothioate R_P,S_P-**8a** was prepared from phenyldichlorophosphine by the following sequence of reactions. Phenyldichlorophosphine when allowed to react with *l*-(-)-menthol in pyridine solutions gave the crude *O-l*-(-)-menthyl-P-phenylphosphonochloridite R_P,S_P-**10a**. The latter compound was converted into the hydrogen *O-l*-(-)-menthyl-P-phenylphosphinothioate R_P,S_P-**8a** by reaction with hydrogen sulfide. The overall yield, when both reactions were performed as a one-flask procedure, was very high.*



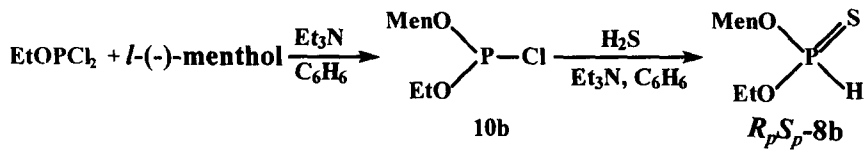
***l*-(-)-menthol** **10a** R_pS_p-**8a**

8a was obtained as a mixture of diastereomers S_P,R_P.[6] The thick pale liquid was separated by crystallisation from n-hexane. The crystalline diastereoisomer S_P-**8a** was filtered off (m.p. 58°-60°C, δ^{31}P 63 ppm) and we found that the hexane solution remaining was composed of ca. 80% of diastereomer R_P-**8a** (δ^{31}P 58 ppm) and 20% of S_P-**8a** (δ^{31}P 63 ppm). The R_P-**8a**

* In schemes throughout this paper Men refers to the group *l*-(-)menthyl derived from *l*-(-)menthol.

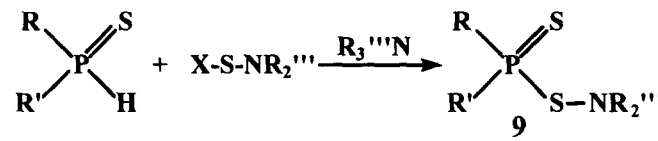
diastereomer seems be thermodynamically less stable and readily rearranges thermally, or under influence of protic acids or amonia, into a 1:1 mixture of R_P-**8a** and S_P-**8a**. Therefore it is possible to transform a mixture of diastereomers R_P,S_P-**8a** (1:1) very efficiently into the single diastereomer S_P-**8a**. At present we cannot give any rational explanation for this facile epimerization. The absolute configuration of S_P-**8a** has been established by chemical correlation and X-ray crystallography.

Hydrogen *O*-ethyl-*O*-*l*-(-)menthylphosphorothioate **8b**, analogous to **8a** but containing the ethoxy ligand instead of the phenyl one, was prepared by a similar procedure.[8]

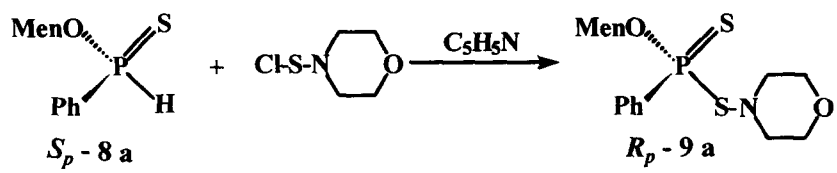


Attempts to separate the R_P,S_P-**8b** mixture into single diastereomers failed.

Synthesis of compounds **8a** and **8b** was undertaken with the intention of using them as intermediates in the synthesis of diastereomeric amidates **9**.

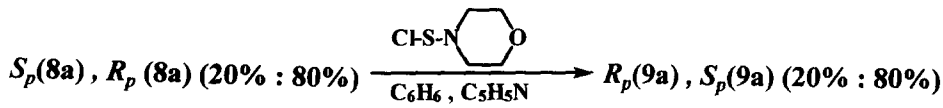


This type of reaction is known to proceed smoothly under mild conditions. The condensation of S_P-**8a** with morpholinesulfenyl chloride proceeds in the presence of pyridine in almost quantitative yield.

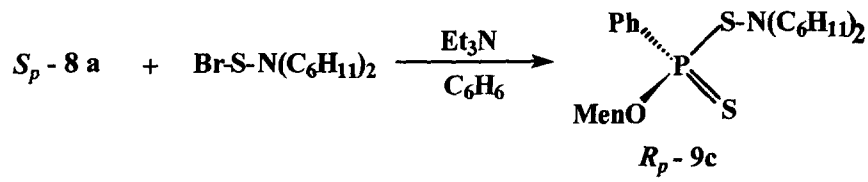


The syrup obtained after separation of triethylamine hydrochloride could not be transformed into the crystalline form of R_P-**9a**. Elemental analysis and ^{1}H and ^{31}P NMR spectroscopy all showed it was of high purity. ^{31}P NMR spectra showed clearly the structure and purity of diastereoisomeric **8a** and **9a**, and were found to be most convenient for analysing diastereoisomers described throughout this paper.

The mixture of diastereomers S_P-**8a** and R_P-**8a** (20:80) which remained after separation of the crystalline S_P-**8a** was allowed to react with morpholinesulfenyl chloride in benzene solution. A mixture of sulfenamides R_P-**9a** and S_P-**9a** was formed in the same ratio (20:80) as that observed for the starting materials S_P-**8a** and R_P-**8a**.

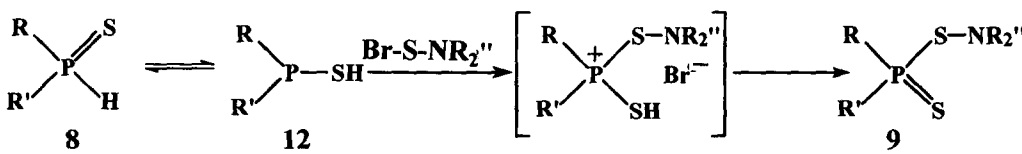


We decided to prepare the crystalline sulfenamides S_P-**9a** derived from dicyclohexylamine. Attempts to prepare the required dicyclohexylaminesulfenyl chloride $(C_6H_{11})_2N$-SCl by chlorinolysis of the disulfide $[(C_6H_{11})_2$-$S]_2$ failed to give a product of reasonable purity. In contrast bromolysis of this disulfide gave dicyclohexylaminosulfenyl bromide of high purity. The bromide was condensed with S_P-**8a** in the presence of triethylamine to give crystalline dicyclohexylsulfenamide R_P-**9c** in almost quantitative yield.



The R configuration in R_P-**9c** prepared as described above was established by X-ray analysis and indicates unambiguously that the reaction proceeds with retention of configuration at the chiral phosphorus center.[9]

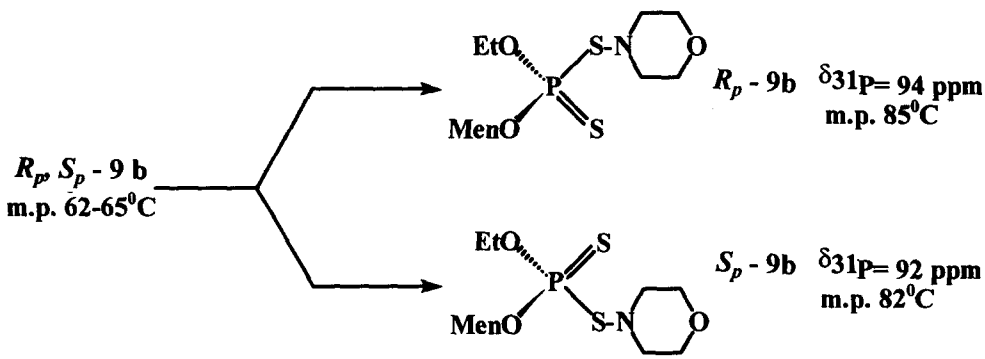
The likely mechanistic scheme for the above reaction involves attack of electrophilic sulfur on the tricoordinate tautomeric form **12** of the compound **8** to form the phosphonium intermediate, which is immediately transformed by proton abstraction into the sulfenamide **9**.



Retention of configuration at the phosphorus center is in agreement with this scheme.

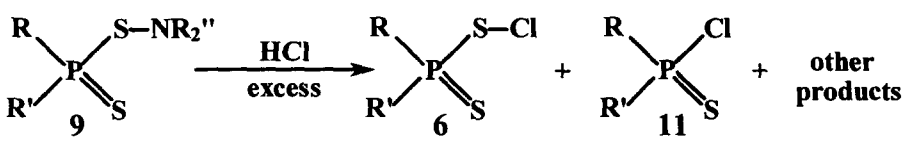
Synthesis of the ethoxy-*l*-(-)-menthoxy thioxophosphoranesulfenmorpholidates **9b** was successfully carried out by the same strategy used for compounds **9a** and **9c**. Crude ethyl-*l*-(-)-

menthylphosphorochloridite **10b** was prepared from *l*-(-)-menthol and ethylphosphorodichloridite $EtOPCl_2$ and converted into the mixture of hydrogen ethyl-*l*-(-)-menthylphosphonothioates R_P,S_P-**8b** by reaction with hydrogen sulfide in the presence of triethylamine. Our attempts to separate the mixture of diastereoisomers **8b** failed. Luckily the reaction of diastereoisomers R_P,S_P-**8b** with morpholinesulfenyl chloride gave a crystalline product R_P,S_P-**9b** which was separated into pure diastereoisomeric sulfenamides R_P-**9b** and S_P-**9b** by crystallization from ethanol. They can be readily characterised by their ^{31}P NMR spectra which reveal the purity of the single diastereomer. The diastereoisomeric purity of compounds R_P-**9b** and S_P-**9b** can be estimated from the melting point; even a small admixture of the second diastereoisomer results in considerable depression of the melting point and lack of sharpness. The absolute configuration of the sulfenamides **9b** was established by X-ray crystallography.[10]



Synthesis of Diastereomeric Thioxophosphoranesulfenyl Chlorides 6a,b.

Synthesis of thioxophosphoranesulfenyl chlorides **6**, based on the reaction of sulfenamides **9** with hydrogen chloride, has been described by Almasi.[11]

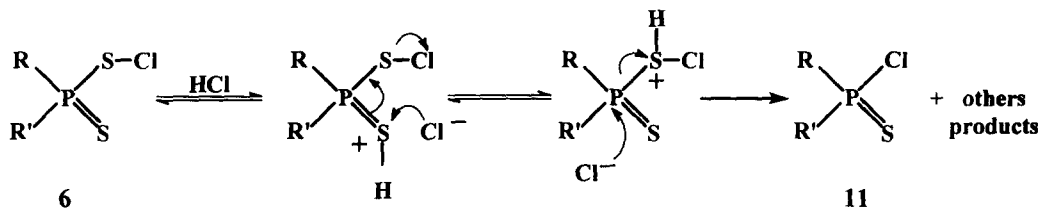


In spite of our best efforts, this method of synthesis of thioxophosphoranesulfenyl chlorides **6** did not give yields in excess of 60%. Considerable amounts of thionochlorides **11** were invariably observed. Formation of elemental sulfur and sulfur chlorides was also observed.

What is more, this reaction leads to 50:50 mixtures of diastereomers when applied to particular diastereomeric sulfenamides **9**. For example, this occurred when diastereomer R_P-**9a** was allowed to react with hydrogen chloride.

$$R_p\text{-}9a \xrightarrow[\text{excess}]{\text{HCl}} R_p, S_p\text{-}6a + \underset{\textbf{11a}}{\text{Ph(MenO)P(S)Cl}}$$

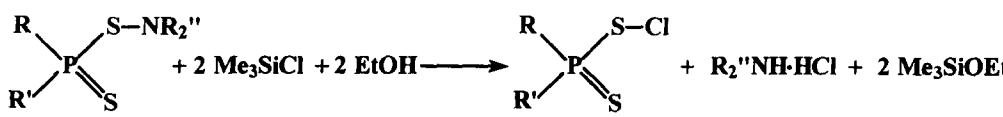
According to our investigations formation of the thionochlorides **11** is caused by the reaction of sulfenylchlorides **6** with hydrogen chloride. Our tentative explanation is based on the assumption that the sulfur center is protonated and chloride anion subsequently attacks either the sulfur or the phosphorus center.



6 **H** **11**

The reversibility of the first step explains loss of stereochemical integrity of compounds **6**. In our previous studies we had noticed that chlorination of dithioacids of phosphorus proceeds with formation of thionochlorides **11**.[12] Because of the achiral nature of the assumed intermediate, **11** must be formed as a mixture of the corresponding diastereomers (50:50).

After further work we were able to find a suitable experimental procedure for conversion of the thioxophosphoranesulfenylamides **9** into the corresponding sulfenyl chlorides **6** exclusively and with full preservation of stereochemical integrity at the chiral P-center. The secret is to allow sulfenamides **9** to react with trimethylchlorosilane (TMCS) in the presence of ethyl alcohol.



9 **6**

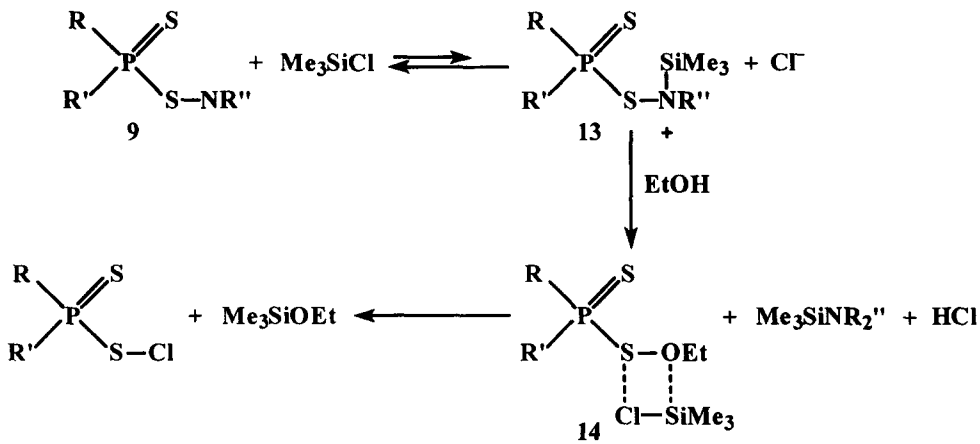
According to our observations trimethylchlorosilane does not react with amidates **9** to form sulfenyl chlorides **6**. Participation of ethyl alcohol in the process leading to chlorides **6** can be explained by the formation of hydrogen chloride in the reaction of ethyl alcohol with

trimethylchlorosilane. This reaction is known to be extremely slow unless a suitable catalyst, such as dimethylsulfoxide, is present.[13] If the reaction between TMCS and EtOH is assumed to be reversible, with the equilibrium strongly shifted toward the substrates, the sulfenamide may act as hydrogen chloride scavenger.

$$ROH + Me_3SiCl \rightleftharpoons R\,OSiMe_3 + HCl$$

Thus in this procedure no excess of hydrogen chloride is present which could effect epimerization and formation of side products.

Another speculative explanation is based on the assumption that the trimethylchlorosilane TMCS reacts with sulfenamides **9** to give the ammonium salt **13**.

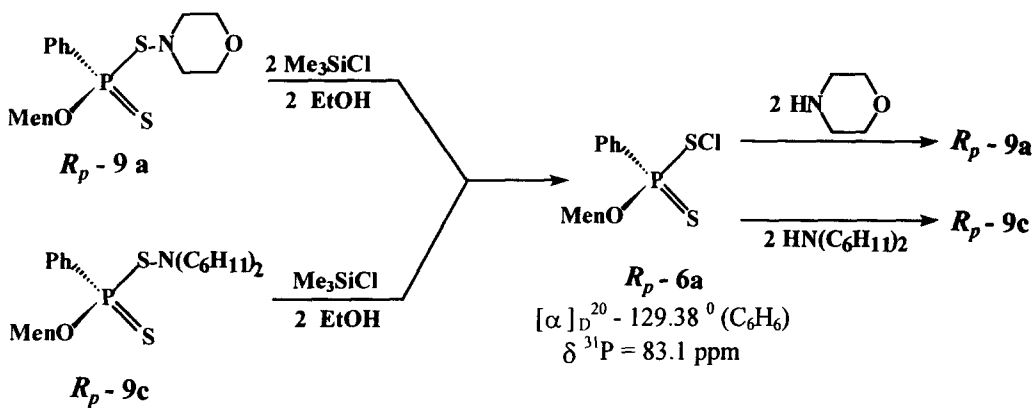


$$Me_3SiNR'' + HCl \longrightarrow Me_3SiCl + R_2''NH{\cdot}HCl$$

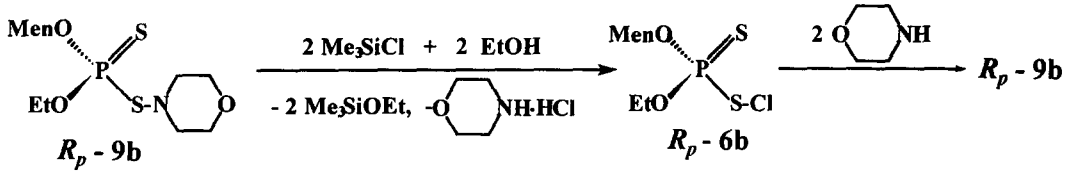
The salt **13** reacts with ethanol to yield the sulfenic ester **14** which reacts smoothly with regenerated TMCS to give the desired sulphenyl chloride **6**. Both explanations account for the very high stereochemical purity of diastereomeric sulfenyl chlorides **6** in the reaction with TMCS in the presence of ethanol.

This advantageous method of synthesis of sulfenyl chlorides **6** secures high yield and purity of simple compounds like diethoxythioxophosphoranesulfenyl chlorides **6** (R=R'=OEt) as well as more complex systems containing P-chiral centers.

The sulfenyl chlorides S_P-**6a**, S_P-**6b**, R_P-**6b** are formed in almost quantitative yield from the corresponding sulfenamidites R_P-**9a**, R_P-**9c**, R_P-**9b** and S_P-**9b**.

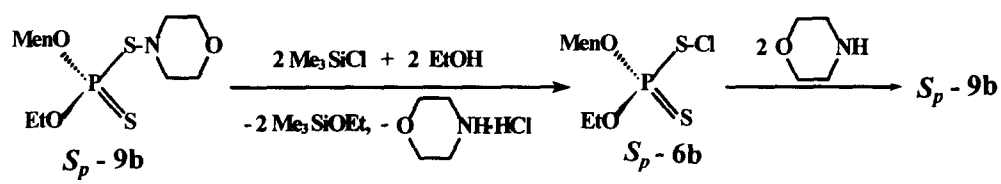


[α]D20 - 93 0 (C6H6)
δ 31P = 91.3 ppm



[α]D20 - 27.5 0 (C6H6)
δ 31P = 94 ppm
m.p.80 0C

[α]D20 - 89.5 0 (C6H6)
δ 31P = 77 ppm



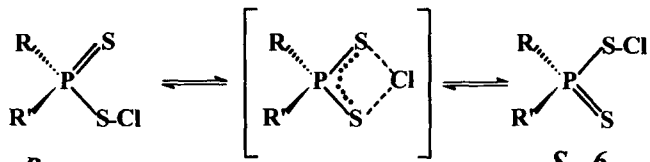
[α]D20 - 52.2 0 (C6H6)
δ 31P = 92 ppm
m.p.82 0C

[α]D20 - 53.2 0 (hexane)
δ 31P = 76 ppm

Our assumption that the P-chiral sulfenyl chlorides **6** may serve as a stereochemical probe for displacement reactions occurring at dicoordinate sulfur in this type of compound is fully confirmed as regards their reactions with secondary amines. These displacement reactions proceed with almost complete stereochemical integrity at the phosphorus atom. These observations suggest a synchronous mechanism of bond breaking and bond formation during nucleophilic displacement at the dico-ordinate sulphur atom. The same can be said of the

reaction of sulphenamides **9** with hydrogen chloride. Even though the achiral nature of dicoordinate sulphur precludes any direct investigation of the stereochemistry of nucleophilic substitution at sulphenyl sulphur, our stereochemical results corroborate mechanistic views derived from the kinetic studies. This result does not support either ionic or radical mechanisms.

The stereochemical stability of the sulfenyl chlorides **6** excludes halotropy or the symmetrical structure of the type **15**.



R_p - 6 **15** S_p -6

In conclusion: It has been demonstrated that the P-chiral sulfenyl chlorides **6a,b** can be prepared in a stereospecific way from the corresponding P-chiral sulfenamides **9a,b,c**. The latter compounds have been converted back stereospecifically into the P-chiral chlorides **6**. These results show that P-chiral sulfenyl chlorides **6a,b** can be employed as stereochemical probes for displacement reactions with amines at dicoordinate sulfur in this type of compounds.

EXPERIMENTAL

The solvents were reagent grade and were distilled and dried by conventional methods before use. ^{1}HNMR spectra were recorded at 300 MHz with Bruker AC 200 and Bruker MSL-300 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 TMS. ^{31}PNMR spectra were obtained on the same instruments operating at 81.1 MHz and 121.4 MHz respectively. Frequency being observed for saturated solutions with external 85% H_3PO_4. Optical rotations were measured on a Perkin -Elmer 241 MC polarimeter. Melting points were determined on a Boetius PHMK apparatus and are uncorrected. Ethylphosphorodichloridite, was synthesized according to the described procedure [14].

Synthesis of R_P,S_P Hydrogen *O*-ethyl *O*-*l*-(-)-menthylphosphinothioate (8b)

To a solution of 73.5g (500 mmol) the ethylphosphorodichloridite in 300 ml hexane, was added dropwise with stirring at temperature -10^{0}C , the solution of 78g (500 mmol) of *l*-(-)-menthol , triethylamine 101.2g (1000 mmol) in 300ml hexane. After the addition was complete , the cooling bath was removed and the temperature was increased slowly to 15^{0}C. The stirring was continued for 1hr at 15-20^{0}C and next through the reaction solution a stream of dry hydrogen sulfide was passed slowly for 5hr at temperature 0-5^{0}C. The triethylamine hydrochloride was filtered off. The solvent was evaporated and the residual liquid was fractionated. The oily liquid, 125 g, yield 94%, bp. 75^{0}C/0.05 mmHg; ^{31}PNMR ($CDCl_3$) two lines 60.0 ppm; 65.1 ppm , ratio (1:1); $^1J_{P\text{-}H}$ 647 Hz ; Anal. Calcd. for $C_{12}H_{25}O_2PS$: C, 54.52; H, 9.53; P., 11.72; S, 12.10. Found: C, 54.45; H, 9,20; P., 11.86; S, 11.40.

Synthesis of R_P Morpholinosulfenyl [(-)p-menthan-3-yloxy] phenylthioxo-phosphorane (9a)

To a stirred solution of 2.96g (10mmol) of S_P-**8a**[7] and 1.0g (10mmol) of triethylamine in 50 ml hexane was added at a temperature of -20^{0}C the solution of 1.53g (10mmol) of morpholinesulfenyl chloride in 5 ml hexane. The stirring was continued for 1hr at room temperature and the precipitated hydrochloride was removed by filtration. The solvent was evaporated and residual liquid was evaporated at pressure 1-2 mmHg at 20^{0}C for 1hr. The oily liquid, 4.13g, 99% yield was obtained. ^{31}PNMR ($CDCl_3$) 91.3 ppm; ^{1}HNMR ($CDCl_3$) 7.96-7.36 (m.,Ph, 5H); 4.62-4.57 (m.,OCH, 1H); 3.67-2.60 (m., 9H); 0.88 (d, CH_3CH_3CH, 3H, $^3J_{H\text{-}H}$ 7Hz); 0.83 (d CH_3CH_3CH, 3H, $^3J_{H\text{-}H}$ 7Hz); 0.76 (d,CH_3, $^3J_{H\text{-}H}$ 6.5 Hz); [α]$_D^{20}$ - 92.63 (c, 2.1, benzene); Anal. Calcd. for $C_{20}H_{32}NO_2PS_2$: C, 58.08; H, 7.80: P., 7.49; S, 15.5. Found: C, 58.18; H, 7.78; P, 6.88; S, 13.76; N, 3.92.

Reaction of mixture (80:20) of R_P,S_P Hydrogen O-*l*-(-)-menthylphenyl-phosphinothioate (8a) with morpholinesulfenyl chloride

Under identical reaction conditions as was described for the synthesis of R_P-**9a**, the reaction between of a mixture of **8a**, containing 80% of the R_P isomer ^{31}Pδ 58.0 ppm and 20% of the

isomer S_P (^{31}Pδ 63.0 ppm) and morpholinesulfenyl chloride in hexane solution in the presence of triethylamine, gave a mixture of isomeric sulfenamides of S_P-**9a**, ^{31}Pδ 90.0 ppm (80%) and R_P-**9a** ^{31}Pδ 91.3 ppm (20%) as a oily liquid in 98% yield

Reaction of R_P,S_P Hydrogen *O*-ethyl, *O*-*l*-(-)-menthylphosphorothioate (8b) with morpholinesulfenyl chloride.

The solution of 26.4g (100 mmol) the R_P,S_P- **8b** (1:1 ratio by ^{31}PNMR) and 10.1g (100 mmol) of triethylamine in 150 ml hexane, was treated with stirring at temperature -15^{0}C, with 15.3g (100 mmol) of morpholinesulfenyl chloride dissolved in 50 ml hexane. The cooling bath was removed and the reaction mixture was stirred for 2 hr. The hydrochloride was filtered off and the solvent was evaporated *in vacuo* to yield.The solid residue, 35g, 92% yield as the mixture of isomeric sulfenamides **9b**, δ^{31}P94.0 ppm and 92.1 ppm in ratio 1:1. After fractional crystallization the 3.81g sample of **9b** from ethanol, two products were separated : (i) 1.5g of S_P-**9b**, mp.82^{0}C; $[\alpha]_D^{20}$ -52.2 (c, 2.1, benzene); ^{31}P NMR(C_6H_6) 92.1 ppm; Anal.Calcd. for $C_{16}H_{32}NO_3PS_2$: C, 50.38; H, 8.45; P., 8.12; S,16.77; N, 3.67. Found: C, 50.50; H, 8.21; P, 8.14; S, 16.85; N, 3.63; (ii) 1.2g of R_P-**9b**, mp. 85^{0}C; $[\alpha]_D^{20}$ -27.5 (c, 2.5, benzene); ^{31}PNMR(C_6H_6) 93.6; Anal. Calcd. for $C_{16}H_{32}NO_3PS_2$: C, 50.38; H, 8.45; P., 8.12; S,16.77; N, 3.67. Found: C, 50.42; H, 8.51; P., 8.16; S, 16.39; N, 3.82. The absolute configurations of both isomers were established by X-ray crystallography [10].

Reaction of R_P-9a with excess of hydrogen chloride

The solution of 0.41g (1mmol) of R_P-**9a** in 20ml hexane, was saturated at temperature -20^{0}C with dry hydrogen chloride at -20°C. The reaction mixture was filtered in the closed system and analysed immediately by ^{31}PNMR spectroscopy. The following compounds were identified as a product of this reaction: sulfenyl chlorides R_P-**6a**, δ 83.1 ppm and S_P-**6a** δ 81.2 ppm in 1:1 ratio, yield 30%; R_P and S_P-**11a** *O*-*l*-(-)-menthylphenylphosphono-chloridothioate **11a**, δ 84.8 ppm and δ 85.39 ppm, ratio 1:1, yield 15%; 5% of bis[*O*-*l*-(-)menthylphenylthiophosphono]-disulfide δ 86.8 ppm and 5% of unidentified compounds δ 87-91 ppm.

Reaction of R_P-9a with chlorotrimethylsilane/ethanol R_P *O-l*-(-)menthylphenylthioxo-fosforanesulfenyl chloride (6a)

To a stirred solution of 4.1 g (10 mmol) sulfenamide ***R_P*-9a** in 50 ml hexane, was added of 0.92 g (20 mmol) of absolute ethanol at -20°C and then 2.16 g (20 mmol) of freshly distilled chlorotrimethylsilane. The morpholine hydrochloride was filtered off in the closed system. The formation of only one organophosphorus product with chemical shift at δ^{31}P 83.1 ppm (hexane) was confirmed by the ^{31}P NMR spectrum of the reaction solution. The solvent was evaporated at a temperature below 5°C and 3.62 g, yield 100% of a yellow oily liquid was obtained; $[\alpha]_D^{20}$ -129.38 (c, 2.1, benzene), ^{1}H NMR ($CDCl_3$) 8.08-7.4 (m, Ph, 5H); 4.85-4.07 (m, OCH, 1H); 2.51-2.24 (m, CH_3CH_3CH, 1H); 1.74-1.01 (m, 9H); 0.98-0.71 (m, CH_3CH_3CH,CH_3, 9H). The product was identified as ***R_P*-6a** and for further reactions was used in the crude form immediately after synthesis.

Reaction of the sulfenyl chloride R_P-6a with morpholine

From the reaction of 1.81 g (5 mmol) of freshly prepared ***R_P*-6a** δ^{31}P 83.1 with 0.87 g (10 mmol) dry morpholine performed in 40 ml hexane at temperature 0-5°C, the sulfenamide ***R_P*-9a** oily liquid of 2.06 g, yield 100% was obtained. ^{31}P NMR (C_6H_6) 91,3 ppm. Anal.calcd. for $C_{20}H_{32}NO_2PS_2$: C, 58,08; H, 7.80; P, 7.49; S, 15.50; N, 3.39. Found: C, 57.18; H, 7.78; P, 6.98; S, 13.66, N, 3.90.

Reaction of sulfenyl chloride R_P-6a with dicyclohexylamine

To a solution of 1.81 g (5 mmol) ***R_P*-6a** in 40 ml hexane was added with stirring at 0-5°C a solution of 1.81 g (10 mmol) of dicyclohexylamine in 5 ml hexane. The hydrochloride was filtered off and the solvent was evaporated *in vacuo*. The crude sulfenamide ***R_P*-9c** was purified by crystallization from hexane-benzene (3:1), 2.5 g yield 98%, m.p. 99-100°C, $[\alpha]_D^{20}$ +2,31° (c 2.5, chloroforme), ^{31}P NMR (C_6H_6) δ 97.40 ppm. Anal.Calcd. for $C_{28}H_{46}NOPS_2$: C, 65.12; H, 9.15; P, 6.29; S, 13.53; N, 2.71. Found: C, 66.23; H, 9.13; P, 6.10; S, 12.63; N, 2.76.

Reaction of sulfenamide R_P-9c with chlorotrimethylsilane/ethanol

From the reaction of 0.87 g (1.7 mmol) ***R_P*-9c** with 0.14 g (3,4 mmol) of ethanol and 0.36 g (3,4 mmol) chlorotrimethylsilane performed at -15°C in 10 ml hexane, the sulfenyl chloride ***R_P*-6a** ^{31}P NMR (C_6H_6) 83.0 ppm, as a yellow oily liquid of 0.46 g, yield 96% was obtained. $[\alpha]_D^{20}$ - 130.28 (c, 2.2 benzene).

***R_P* *O*-Ethyl *O*-*l*-(-)-methylthioxophosphoranesulfenyl chloride (6b)**

To a solution of 1.9 g (5 mmol) of sulfenamide ***R_P*-9b** in 40 ml hexane was added at room temperature with stirring 0.46 g (10 mmol) of absolute ethanol and next at -40°C, 1.08 g (10 mmol) of freshly distilled chlorotrimethylsilane. The morpholine hydrochloride was filtered off and in the solution, only one organophosphorus product with chemical shift at δ 77 ppm (hexane) was observed by ^{31}P NMR spectroscopy. The solvent was evaporated and 1.65 g of the product ***R_P*-6b** was obtained as a yellow liquid. $[\alpha]_D^{20}$ -89.5 (c, 1.5 benzene). The reaction of this crude product with 0.87 g (10 mmol) of dry morpholine in 40 ml hexane at 0-5°C gave the 1.9 g, yield 100% of the sulfenamide ***R_p*-9b**, m.p. 85°C from absol. EtOH; ^{31}P NMR spectrum ($CDCl_3$) 94 ppm.

***S_P* *O*-Ethyl *O*-*l*-(-)-methylthioxophosphoranesulfenyl chloride (6b)**

The solution of 1.9 g (15 mmol) of the sulfenamide ***S_P*-9b** (δ^{31}P 92 ppm) in 35 ml hexane was treated with stirring at room temperature with 0.46 g (10 mmol) ethanol. To this solution was added dropwise at -40°C 1.08 g (10 mmol) of chlorotrimethylsilane. The precipitated hydrochloride was filtered off and the solvent was evaporated off to 1.65 g, yield 100% of ***S_P*-6b** as a yellow oil. ^{31}P NMR spectrum (hexane) 76 ppm; $[\alpha]_D^{20}$ -53.2° (c, 3.9, hexane).

The product obtained was treated with 0.87 g (10 mmol) of morpholine in 40 ml hexane at 0-5°C. The solvent was evaporated and the crude ***S_p*-9b** was recrystallized from ethanol, 1.9 g, yield 100%; m.p. 82°C, ^{31}P NMR spectrum (C_6H_6) 92.1 ppm; $[\alpha]_D^{20}$ -52.15 (c, 2.5, benzene).

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