# Reaction of Tricoordinate Phosphorus Compounds with Organophosphorus Pseudohalogens. 1. Desulfurization and Deoxygenation of Oxophosphoranesulfenyl Chlorides. Scope and Mechanism†

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The reaction of oxophosphoranesulfenyl chlorides RR'P(O)SCl **2** with $P^{III}$ compounds has been investigated. Its mechanistic features have been elucidated by variable-temperature $^{31}P$ NMR spectroscopy and stereochemical changes at $P^{IV}$ and $P^{III}$ phosphorus centers. These studies show that in all cases phosphonium intermediates containing the sulfur bridge $>P(O)\text{-}S\text{-}\overset{+}{P}< Cl^-$ are formed. Depending on electronic and steric factors and reaction conditions, this primary phosphonium salt either decomposes by nucleophilic attack of the chloride counterion on the phosphoryl center (desulfurization pathway) or is transformed into the isomeric phosphonium salt $>P(S)\text{-}O\text{-}\overset{+}{P}< Cl^-$. The latter decomposes by the attack of the chloride anion on the thiophosphoryl center (deoxygenation pathway). $^{31}P$ NMR studies fully corroborated the observed stereochemical changes.

## Introduction

As a part of a research program on the chemistry and stereochemistry of thio- and selenophosphates, detailed studies have been undertaken on the reactions of pseudohalogens such as thiocyanogen $(SCN)_2$,[1] phosphoryl disulfides $[R_2P(O)S]_2$,[2] phosphoryl diselenides $[R_2P(O)Se]_2$,[2,3] and oxophosphoranesulfenyl halides $R_2P(O)SX$[2,4] with tricoordinate phosphorus compounds.

Organophosphorus disulfides RR'P(O)SSP(O)RR' **1** display a variety of properties similar to those of elemental halogens, and hence the term pseudohalogens or halogenoids has been applied to them.[5] The pseudohalogen behaviour of disulfides **1** was first described by Foss.[6] Oxophosphoranesulfenyl chlorides RR'P(O)SCl **2**, representing pseudohalogenohalogens, were obtained for the first time, and studied, in this laboratory.[7,8]

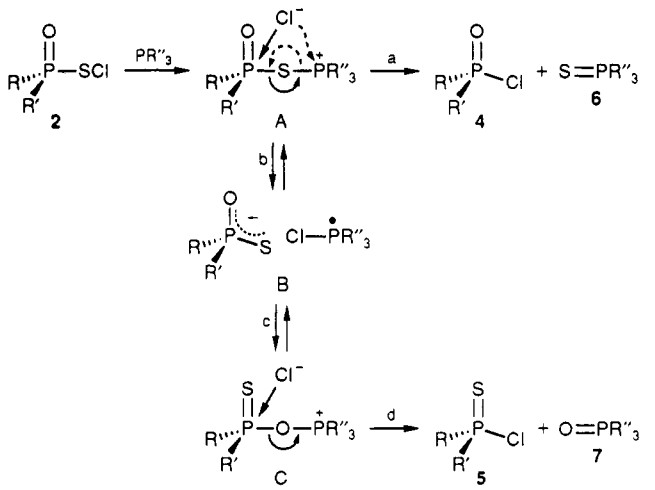
The high affinity of tricoordinate phosphorus compounds toward oxygen and sulfur is based on their tendency to form a strong phosphoryl P=O or thiophosphoryl P=S "double" bond. Desulfurization and deoxygenation reactions by tricoordinate phosphorus compounds are widely used in organic synthesis.[9] Little attention has been paid to the systems containing both "active" O and S atoms. Harpp et al. observed preferential desulfurization of thiolosulfonates $RSO_2SR$ by tris(diethylamino)phosphine.[10] Barton et al. described preferential deoxygenation of sulfenyl esters RS–OR with the triphenylphosphine.[11] Early observations of similar reactions in phosphorus chemistry with parallel desulfurization and deoxygenation of bis(phosphinyl) disulfides **1** by triphenylphosphine have been reported by Edmundson.[12] Michalski and Skowrońska et al. observed deoxygenation, desulfurization and dealkylation of oxophosphoranesulfenyl chlorides **2** by trialkyl phosphites.[4]

We describe the results of systematic studies of the reaction between chiral and nonchiral oxophosphoranesulfenyl chlorides **2** and tricoordinate phosphorus compounds. In these investigations it was essential to combine chemical and stereochemical observations with those derived from variable-temperature $^{31}P$ NMR experiments. Our aim was to disclose mechanistic features of deoxygenation and desulfurization processes of importance for applications in synthetic organophosphorus chemistry.

## Results and Discussion

For our experimental observations and the mechanistic feature of these reactions it is advantageous to examine Scheme I. This scheme provides a general description of

Scheme I



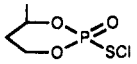
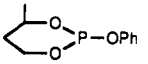
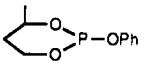
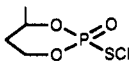
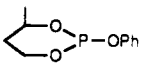
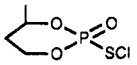
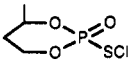
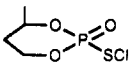
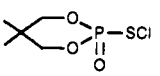
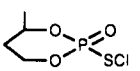

2 A 4 6 B C 5 7

† Dedicated to Professor Frank H. Westheimer on the occasion of his 80th birthday.

(1) Burski, J.; Kieszkowski, J.; Michalski, J.; Pakulski, M.; Skowrońska, A. *Tetrahedron* **1983**, *39*, 4175 and references cited therein.
(2) Skowrońska, A.; Krawczyk, E.; Burski, J. *Phosphorus Sulfur Relat. Elem.* **1983**, *18*, 233 and references cited therein.
(3) Dembiński, R.; Krawczyk, E.; Skowrońska, A. *Phosphorus Sulfur Relat. Elem.* **1988**, *35*, 345.
(4) (a) Michalski, J.; Skowrońska, A. *J. Chem. Soc. C* **1970**, 703. (b) Krawiecka, B.; Michalski, J.; Mikołajczak, J.; Mikołajczyk, M.; Omelańczuk, J.; Skowrońska, A. *J. Chem. Soc., Chem. Commun.* **1974**, 630. (c) Omelańczuk, J.; Kiełbasiński, P.; Michalski, J.; Mikołajczak, J.; Mikołajczyk, M.; Skowrońska, A. *Tetrahedron* **1975**, *31*, 2809. (d) Michalski, J.; Skowrońska, A.; Bodalski, R. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1987; Chapter 8.
(5) (a) Moeller, T. *Inorganic Chemistry*; J. Wiley: New York, 1952. (b) Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1978; p 677.
(6) Foss, O. *Acta Chem. Scand.* **1947**, *1*, 307.
(7) Borecka, B.; Michalski, J. *Roczniki Chem.* **1957**, *31*, 1167. Michalski, J.; Skowrońska, A. *Chem. Ind.* **1958**, 1199. Michalski, J.; Pliszka-Krawiecka, B.; Skowrońska, A. *Roczniki Chem.* **1963**, *37*, 1479.
(8) (a) Michalski, J. *Bull. Soc. Chim. Fr.* **1963**, 11 and references cited therein. (b) Markowska, A.; Michalski, J. *Roczniki Chem.* **1964**, *38*, 1141. (c) Borecka, B.; Jezierska, B.; Bluj, S.; Michalski, J. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1974**, *22*, 201.
(9) (a) Mukaiyama, T.; Takei, H. *Topics in Phosphorus Chemistry*; J. Wiley and Sons: New York, 1976; Vol. VIII, pp 587–645. (b) Corey, E. J.; Brunella, D. J. *Tetrahedron Lett.* **1976**, 3409. (c) Mukaiyama, T.; Matseuda, H.; Suzuki, M. *Tetrahedron Lett.* **1970**, 1901. (d) Cadogan, J. I. *Acc. Chem. Res.* **1972**, *5*, 303. (e) Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: New York, 1979; pp 269–380.
(10) Harpp, D. N.; Gleason, J. G.; Ash, D. K. *J. Org. Chem.* **1971**, *36*, 322.

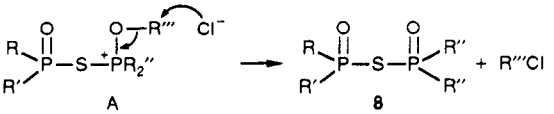
0022-3263/92/1957-4963$03.00/0 

Table I. Desulfurization and Deoxygenation of Sulfenyl Chloride 2 by $P^{III}$ Compounds 3

| entry | sulfenyl chloride 2 | $P^{III}$ compd 3 | desulfurization (%) | deoxygenation (%) |
|---|---|---|---|---|
| 1 | $(EtO)_2P(O)SCl$ | $(Me_3CCH_2O)_3P$ | 100 | 0 |
| 2 | (EtO)EtP(O)SCl | $(Me_3CCH_2O)_3P$ | 100 | 0 |
| 3 |  cis, trans | $(Me_3CCH_2O)_3P$ | 100 | 0 |
| 4 | $(EtO)_2P(O)SCl$ |  trans | 100 | 0 |
| 5 | (EtO)EtP(O)SCl |  trans | 100 | 0 |
| 6 |  cis, trans |  trans | 100 | 0 |
| 7 |  cis, trans | $(Et_2N)_3P$ | 100 | 0 |
| 8 | $(EtO)_2P(O)SCl$ | $Bu_2^tPCl$ | 100 | 0 |
| 9 | $(EtO)_2P(O)SCl$ | $(Et_2N)_3P$ | 94 | 6 |
| 10 | (EtO)EtP(O)SCl | $(Et_2N)_3P$ | 96 | 4 |
| 11 |  cis, trans | $(PhO)_3P$ | 95 | 5 |
| 12 | (EtO)EtP(O)SCl | $(PhO)_3P$ | 92 | 8 |
| 13 | $(EtO)_2P(O)SCl$ | $(PhO)_3P$ | 85 | 15 |
| 14 |  cis, trans | $PCl_3$ | 60 | 40 |
| 15 |  | $PCl_3$ | 60 | 40 |
| 16 | (EtO)EtP(O)SCl | $Ph_3P$ | 60 | 40 |
| 17 |  cis, trans | $Ph_3P$ | 58 | 42 |
| 18 | $(EtO)_2P(O)SCl$ | $Ph_3P$ | 10 (0)[a] | 90 (100)[a] |
| 19 | $(EtO)_2P(O)SCl$ | $PCl_3$ | 5 | 95 |
| 20 | $^t$BuPhP(O)SCl | $Ph_3P$ | 0 | 100 |

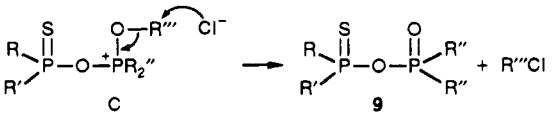
[a] Reaction was carried out at −100 °C.

the desulfurization (path a) and deoxygenation (paths b–d) reactions and contains an essence of our mechanistic interpretation. The pathways a and b–d are representative only for those systems in which ligands at tricoordinate phosphorus are resistant to dealkylation or desilylation. When an alkoxy group OR″ is attached to the $P^{III}$ center the izomeric monothiopyrophosphates 8 and 9 are formed. Formation of 8 results from dealkylation of the intermediate A.



A 8

Similarly, the source of the 9 is dealkylation of the intermediate C.



C 9

In both cases the products of the type 4–7 are also formed. For example, when R, R′ = EtO, R″ = MeO, and R‴ = Me monothiopyrophosphate 8 is formed in 80% yield while when R, R′ = EtO, R″ = EtO, and R‴ = Et 8 is obtained only in 15%.[4a] When the trimethylsiloxy group is present R‴ = $Me_3Si$ the reaction proceeds in a fully regioselective manner yielding 8 in almost quantitative yield.[13] Nucleophilic displacement at silicon by chloride anion in the primary phosphonium salt A occurs much faster than at the methoxyl carbon, phosphoryl, and phosphonium centers.

The reactions of oxophosphoranesulfenyl chlorides 2 with tricoordinate phosphorus compounds 3 are strongly exothermic. Reaction can be observed even at temperatures close to −100 °C. For preparative purposes, dichloromethane is the solvent of choice. Evaluation of the regioselectivity of the reaction for a representative pair of substrates was made in dichloromethane at −20 °C. Reproducibility of results was good. The structure of all products and their proportions were determined by means

(11) Barton, D. H.; Manley, D.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1568.
(12) Edmundson, R. S. *J. Chem. Soc. C* **1967**, 1635.
(13) (a) Skowrońska, A.; Dembiński, R.; Kamiński, R.; Michalski, J. *Tetrahedron Lett.* **1987**, *28*, 4209. (b) Skowrońska, A.; Dembiński, R.; Kamiński, R.; Michalski, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2107.

of $^{31}P$ NMR spectroscopy and GC chromatography and in most cases by comparison with the authentic samples.

Results of the selected reactions of **2** and **3** are presented in Table I and arranged according to decreasing involvement of desulfurization pathway.

The collected data (Table I) reveal that the regioselectivity of the reaction depends on the ligands at the tricoordinate phosphorus atom and to a lesser extent on the substituents at tetracoordinate phosphorus. In general, acyclic and cyclic phosphites (entries 1–6, 11–13) act as selective desulfurization reagents. The same applies to tris(diethylamino)phosphine (**3d**) (entries 7, 9, 10). Triphenylphosphine (**3f**) and phosphorus trichloride (**3g**) act as deoxygenation reagents but their selectivity depends on the structure of the oxophosphoranesulfenyl chloride (entries 14–20). Steric hindrance strongly affects the reaction course. The presence of bulky groups at the tricoordinate phosphorus atom (entry 8) leads to full desulfurization. In contrast, steric hindrance at the sulfenyl chloride phosphorus atom (entry 20) results in full deoxygenation. Temperature has an influence on the regioselectivity of these reactions. For example, when the reaction of sulfenyl chloride **2a** (R = R″ = EtO) with triphenylphosphine (**3f**) was carried out at −20 °C, up to 10% of the products derived from the desulfurization pathway was observed. At −100 °C only deoxygenation reaction took place (entry 18).

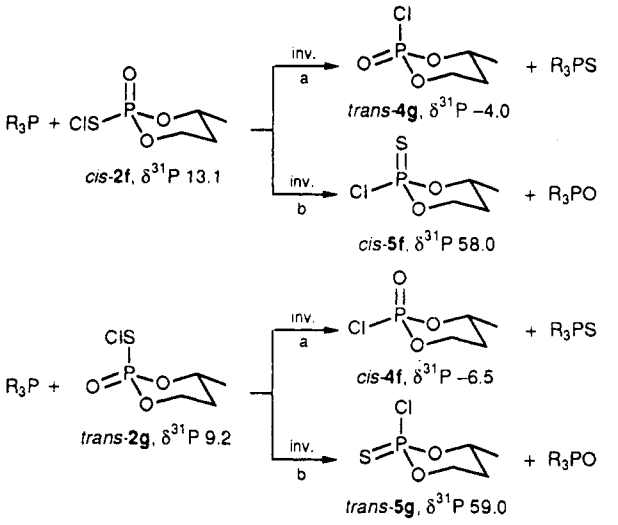
**Stereochemistry.** To study the stereochemistry of the reaction, between sulfenyl chlorides **2** and $P^{III}$ phosphorus compounds the substrates were used in both enantiomeric and diastereomeric forms. Reaction of the optically active oxophosphoranesulfenyl chloride **2b** (R = Et, R′ = EtO) with tricoordinate phosphorus compounds proceeded along pathways a and b–d (Scheme I) yielding a mixture of the optically active acid chlorides **4b** (R = Et, R′ = EtO) and **5b** (R = Et, R′ = EtO).[4b] Both chlorides were formed with inversion of configuration at the phosphorus atom. Their configurational assignments were based on our previous work.[14] However, their optical purity is strongly influenced by the nature of the tricoordinate substrate. Our earlier paper describes that a suitable choice of a tricoordinate compound makes this reaction an excellent method for the highly stereoselective synthesis of thiono chlorides **5** (R = Et, R′ = EtO; R = Me, R′ = $Me_2CHO$; R = $Me_2CH$, R′ = MeO).[4c] The reaction of optically active oxophosphoranesulfenyl chloride **2b** with triphenyl phosphite (**3b**) (Table I, entry 12) proceeds with predominant inversion of configuration at phosphorus atom. This provides a new method of synthesis of the optically active phosphorochloridate **4b**.

The reaction of diastereoisomeric cyclic oxophosphoranesulfenyl chlorides *cis*-**2f** and *trans*-**2g** with trineopentyl phosphite (**3a**), triphenyl phosphite (**3b**), 2-phenoxy-4-methyl-1,3,2-dioxaphosphorinane (*trans*-**3h**), tris(diethylamino)phosphine (**3d**), and triphenylphosphine (**3f**) takes place with inversion of configuration at the phosphorus atom. Fast epimerization into the more stable diastereoizomers of trans configuration[15,19b] is responsible for the low diastereoisomeric purity of 2-chloro-2-thiono-4-methyl-1,3,2-dioxaphosphorinane (*cis*-**5f**) and 2-chloro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (*cis*-**4f**) (Scheme II).

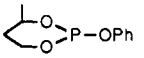
The reaction of the sulfenyl chloride **2a** with diastereoisomeric cyclic phosphites **3i**, **3j**, **3h** and **3k** is fully regio- and stereoselective. Desulfurization proceeds with retention of configuration at the phosphorus atom (Scheme III).

(14) Michalski, J.; Mikołajczyk, M. *Tetrahedron* **1966**, *22*, 3055.

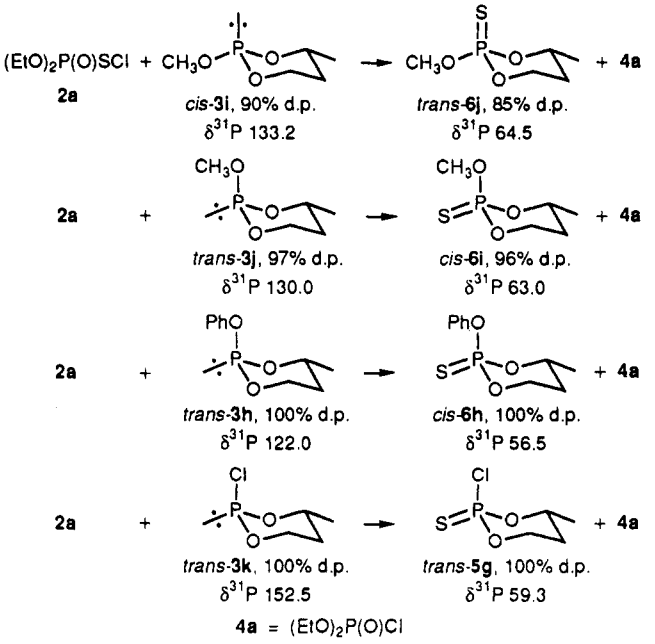
**Scheme II**




diastereoisomeric purity, %

| $R_3P$ | 2 | 4 | 5 |
|---|---|---|---|
| $(Me_3CCH_2O)_3P$ | f 87<br>g 96 | g 92<br>f 66 | |
| $(Ph_3O)_3P$ | f 75<br>g 97 | g 94<br>f 43 | f 60<br>g 94 |
| $(Me_3N)_3P$ | f 87<br>g 90 | g 92<br>f 86 | |
| $Ph_3P$ | f 78<br>g 96 | g 81<br>f 60 | f 34<br>g 96 |
|  trans | f 76<br>g 97 | g 92<br>f 53 | |

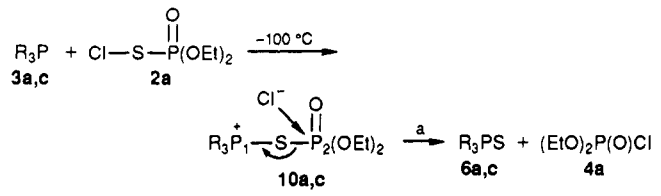
**Scheme III**




Determination of stereochemical changes presented in Schemes II and III was based on $^{31}P$ NMR spectroscopic data available from earlier work by Simpson,[16] Aksnes,[17]

(15) Mikołajczyk, M.; Krzywański, J.; Zimnicka, B. *Phosphorus* **1974**, *5*, 67.
(16) Bodkin, C. L.; Simpson, P. *J. Chem. Soc. B* **1971**, 1136.
(17) Aksnes, G.; Erikson, R.; Mellinger, K. *Acta Chem. Scand.* **1967**, *21*, 1028.

**Scheme IV**




**3a**, R = $Me_3CCH_2O$

**3c**, R = $Me_2N$

**10a**, $\delta$ $^{31}P_1$ 33.3 (d), $P_2$ 4.7 (d) ($J_{PP}$ = 9.7 Hz)

**10c**, $\delta$ $^{31}P_1$ 56.8 (d), $P_2$ 10.6 (d) ($J_{PP}$ = 9.8 Hz)

Stec and Mikołajczyk,[15,18,19] and Michalski and Skowrońska.[20] A more detailed discussion of stereochemistry of the reaction between $P^{III}$ compounds and oxophosphoranesulfenyl chlorides **2** is presented in the section of low-temperature $^{31}P$ NMR studies.

**Variable-Temperature $^{31}P$ NMR Studies.** The application of variable-temperature $^{31}P$ NMR provided important information about the short-lived intermediates involved in the desulfurization and deoxygenation processes. This technique enabled us to establish the effect of substituents at both phosphorus atoms and the effect of reaction conditions on the selectivity of the reaction. $^{31}P$ NMR studies of the reacting systems were carried out in the temperature range −100 to +20 °C in methylene chloride or ethyl chloride. Substrates dissolved in the appropriate solvent were cooled in liquid nitrogen under dry argon and then mixed together. The spectra were monitored at 10-min intervals. Concentration of starting materials, intermediates and final products was estimated by integration of the corresponding signals. For clarity, the number of spectral data presented is reduced to a necessary minimum. Only the data reproducible in at least two experiments are presented.

Reactions between sulfenyl chlorides **2a** and either trineopentyl phosphite (**3a**) or tris(dimethylamino)phosphine (**3c**) proceed with desulfurization. The thermally labile complexes **10a** and **10c** were detected at −100 °C in the ethyl chloride solution.

Clean decomposition of **10a** and **10c** which involves the nucleophilic attack of the counterion on the phosphoryl center leads to the final products: phosphorochloridate **4a** and trineopentylphosphorothioate (**6a**) or the hexamethylamide of thiophosphoric acid (**6c**). The thermal stability of **10a** was distinctly lower than that of **10c**; **10a** decomposes at −70 °C while **10c** is stable up to 0 °C.

In spite of its greater complexity, the nature of the deoxygenation has also been elucidated. $^{31}P$ NMR studies reveal individual stages in the reaction of oxophosphoranesulfenyl chlorides **2** with tricoordinate phosphorus deoxygenation reagents. The reaction between **2a** and triphenylphosphine (**3f**) served as a model.

In this case, the $^{31}P$ NMR spectra at −100 °C confirmed the presence of two intermediate salts **10f** and **11f**. The salt **10f** is similar to salts observed in the reaction of **3a** and **3c** with **2a**. The salt **11f** is a phosphonium salt containing two phosphorus atoms bridged by an oxygen atom. When the reaction is kept at −100 °C for a period sufficient to allow transformation of the substrates into phosphonium salt **10f** and subsequently into salt **11f** (steps a–c, Scheme V), the products are not those of desulfurization. When the temperature rises **11f** decomposes to the deoxygenation products: phosphorochloridothioate **5a** and triphenylphosphine oxide (**7f**) (step d, Scheme V). $^{31}P$ NMR spectrum (a) of the selective deoxygenation reaction of **2a** with triphenylphosphine (**3f**) is shown in Figure 1. The phosphonium salt structure of the intermediates is evident from the $^{31}P$ NMR data. In the spectral data given in Schemes IV and V for the salts **10a,c**, **10f**, and **11f**, a characteristic double doublet appeared due to spin–spin

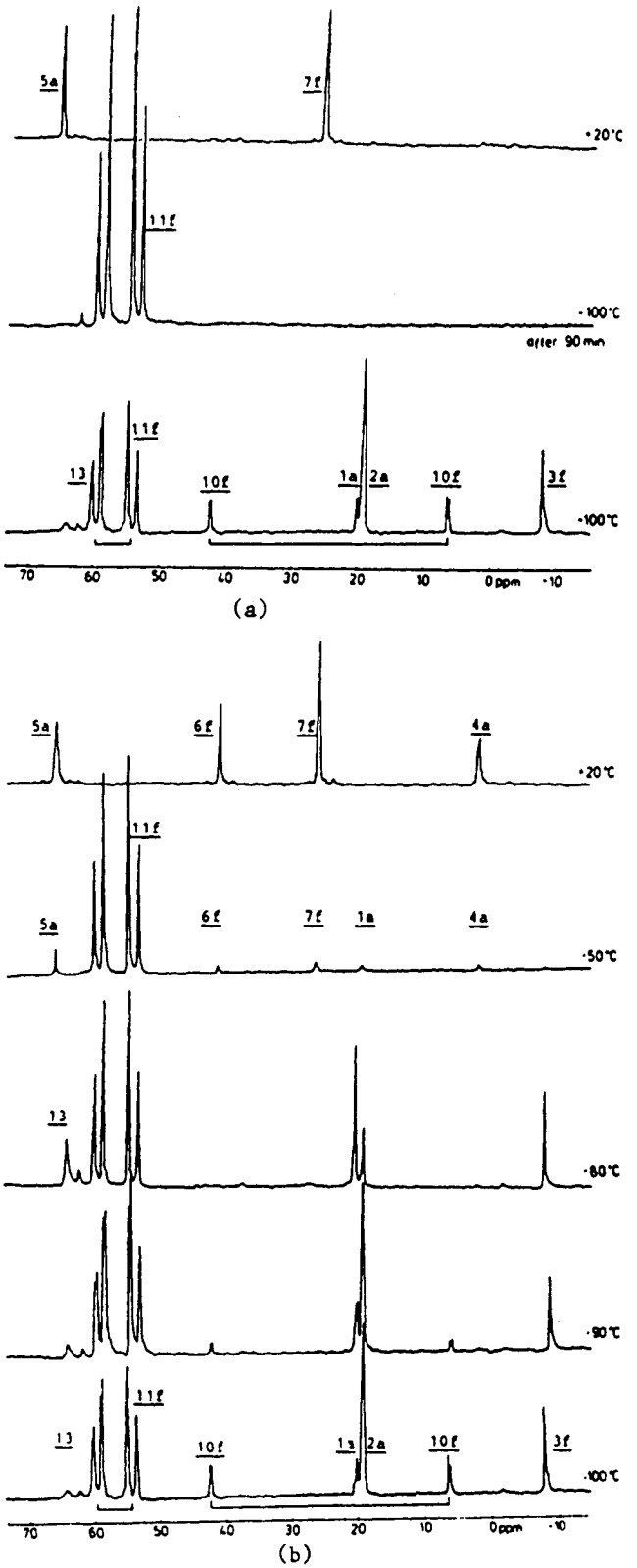


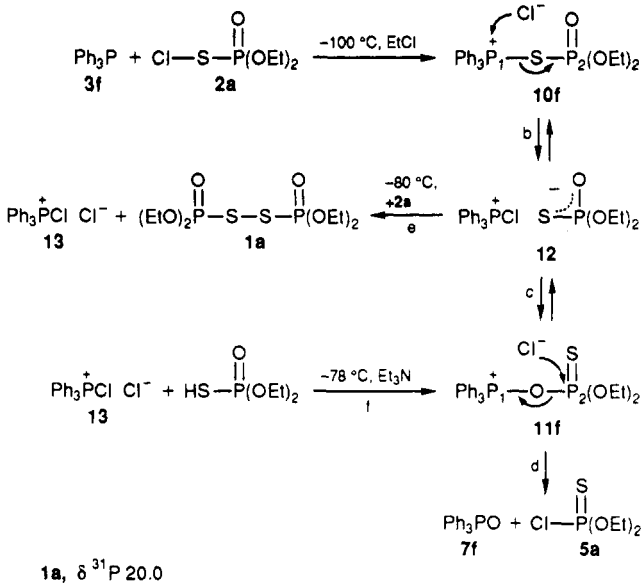

**Figure 1.** $^{1}H$-Decoupled $^{31}P$ NMR spectra (a) and (b) of an equimolar mixture of $(EtO)_2P(O)SCl$ (**2a**) and $Ph_3P$ (**3f**) in ethyl chloride solution recorded at −100 to +20 °C.

(18) Mikołajczyk, M.; Łuczak, J. *Tetrahedron* **1972**, *28*, 5411.

(19) (a) Stec, W. J.; Uznański, B.; Michalski, J. *Phosphorus* **1973**, *2*, 235. (b) Stec, W. J.; Mikołajczyk, M. *Tetrahedron* **1973**, *29*, 539.

(20) Michalski, J.; Mikołajczak, J.; Skowrońska, A. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1973**, *21*, 451.

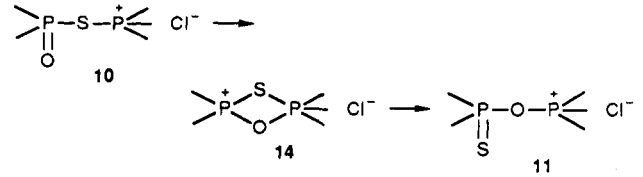
**Scheme V**




**1a**, $\delta^{31}P$ 20.0
**13**, $\delta^{31}P$ 65.5
**10f**, $\delta^{31}P_1$ 42.9 (d), $P_2$ 6.6 (d) ($J_{PP}$ = 11.7 Hz)
**11f**, $\delta^{31}P_1$ 59.5 (d), $P_2$ 54.3 (d) ($J_{PP}$ = 33.2 Hz) (AB) (via steps a–c)
$\delta^{31}P_1$ 59.2 (d), $P_2$ 54.1 (d) ($J_{PP}$ = 33 Hz) (AB) (via step f)

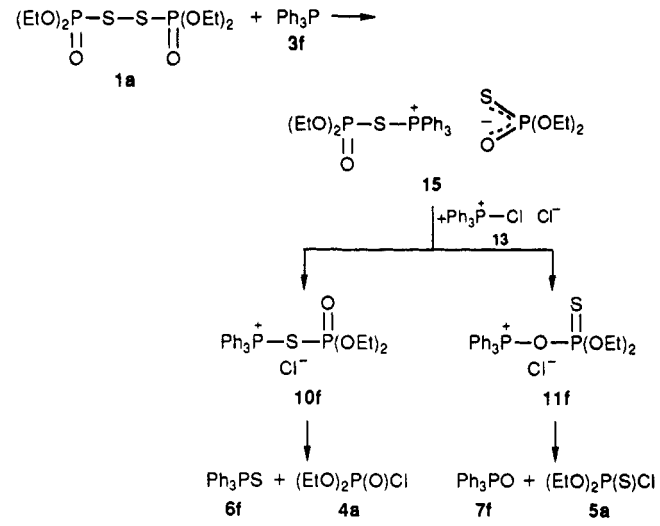
coupling between two nonequivalent phosphorus atoms. The chemical shifts of salts **10a,c**, **10f**, and **11f** were observed in the range expected for phosphonium–phosphoryl centers bridged by sulfur atom and phosphonium–thiophosphoryl centers bridged by oxygen. The lower values of the coupling constant in **10a,c** and **10f**, when compared with **11f**, are in agreement with the observed values for symmetrical RRP(O)SP(O)R′R′ and asymmetrical RRP(S)O–P(O)R′R′ thiopyrophosphates.[21] The structure of the intermediate **11f** containing an oxygen bridge between thiophosphoryl and phosphonium centers was additionally confirmed by the independent synthesis from chlorophosphonium salt **13** and diethylphosphorothioic acid in the presence of triethylamine (step f, Scheme V). The spectral properties of **11f** prepared this way were identical to those of the intermediate **11f**, described in the Scheme V (steps a–c). It is noteworthy that intermediates **10a,c,f** constitute a new type of phosphonium salts containing two phosphorus atoms linked by a sulfur bridge.

It is apparent that the transformation of the phosphonium salt **10f** to the salt **11f** is due to double nucleophilic ligand exchange at the phosphonium phosphorus center (steps b and c, Scheme V). Step c proceeds according to the HSAB principle with the formation of a stronger phosphorus–oxygen bond. When the substituents around the phosphonium center have a stabilizing effect on the pentacoordinate phosphorus structure[4c] participation of the conversion of **10** into **11** through a cyclic complex **14** cannot be excluded. Such isomerization involves a nucleophilic attack of the phosphoryl oxygen at the phosphonium phosphorus atom of **10**:

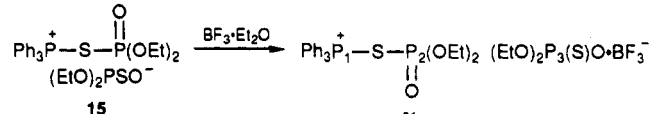



(21) (a) Michalski, J.; Młotkowska, B.; Skowrońska, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 319. (b) Krawczyk, E.; Michalski, J.; Pakulski, M.; Skowrońska, A. *Tetrahedron Lett.* **1977**, 2019.

**Scheme VI**



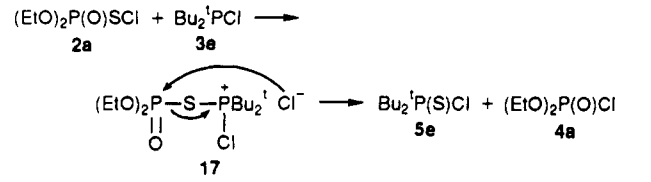

$^{31}P$ NMR spectroscopy was used to follow the formation of products of the desulfurization pathway in the reaction of **2** with triphenylphosphine when the temperature exceeded −100 °C. At −90 °C the substrates **3f** and **2a** were present in the reaction medium, together with the salts **10f** and **11f**. Formation of the disulfide **1a** and the chlorophosphonium salt **13** resulted in the reaction of the salt **12** with the starting sulfenyl chloride **2a** (Scheme V, step e). **12** is a transient species between **10f** and **11f**. Both substrates disappeared at temperatures exceeding −50 °C. At 0 °C the reaction mixture consisted of the final products: phosphorochloridate **4a**, phosphorochloridothioate **5a**, triphenylphosphine sulfide (**6f**), and triphenylphosphine oxide (**7f**). The $^{31}P$ NMR spectrum (b) of nonselective deoxygenation reactions of **2a** with triphenylphosphine (**3f**) is shown in Figure 1. In an additional experiment we have demonstrated that indeed the sulfide **1a** reacts with triphenylphosphine (**3f**) in the presence of chlorophosphonium salt **13** to give the mixture of products resulting from deoxygenation and desulfurization pathways. This observation can be rationalized by assuming that the intermediate phosphonium salt **15** is formed in the reaction between the disulfide **1a** and triphenylphosphine (**3f**).[2] **15** reacts then with chlorophosphonium chloride **13** to give two phosphonium salts **10f** and **11f**, which are crucial intermediates in the formation of the final products (Scheme VI). The involvement of **15** in the reaction of the disulfide **1a** with **3f** has been confirmed by trapping salt **15** with the boron trifluorate etherate at −80 °C; the complex **16** was formed.



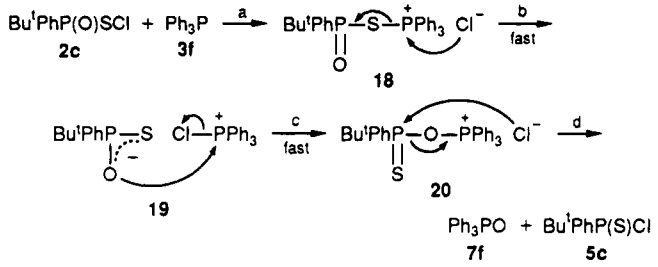

**16**, $\delta^{31}P_1$ 42.6 (d), $P_2$ 6.8 (d), $P_3$ 60.8 (br s) ($J_{PP}$ = 11.8 Hz)

The presence of the phosphonium salts A–C as intermediates (Scheme I) is in accord with the stereochemical results. In the case of the desulfurization reaction there is no bond breaking during the formation of the phosphonium salt A. Consequently, retention of configuration is to be expected. The salt A decomposes by the attack of chloride anion on the phosphoryl center (path a, Schemes I and IV). The strongly electronegative ligands >P-S and Cl are most likely placed in the apical positions of the transition state or in the pentacoordinate interme-

Scheme VII



Scheme VIII



diate. This explains the observed inversion of configuration at the phosphoryl center and retention of configuration at the phosphonium center. The phosphonium group acts as an excellent leaving group. In the case of deoxygenation the salt A is transformed preferentially into the salt B. The latter undergoes a ligand exchange reaction leading to the phosphonium salt C (steps b and c, Schemes I and V). There is no bond breakage at the chiral phosphorus atom during the double consecutive ligands exchange. Therefore, the phosphoryl center of the salt C has the same configuration as the starting sulfenyl chloride **2b**. Finally, the salt C decomposes via nucleophilic displacement at the thiophosphoryl center with the inversion of configuration leading to the compounds **5** and **7** (step d, Scheme V).

**Effect of the Steric Hindrance at Phosphorus Centers.** Decisive influence of the steric effect on the course of reaction between sulfenyl chlorides **2** and tricoordinate phosphorus compounds is in full agreement with the reaction proposed in Scheme I on the basis of the spectroscopic studies. Representative cases of the steric selection are presented in Schemes VII and VIII. The intermediate phosphonium salt **17** formed in the reaction of diethoxyoxophosphoranesulfenyl chloride (**2a**) with di-*tert*-butylchlorophosphine (**3e**) decomposes by the selective nucleophilic attack of the chloride anion on the unhindered phosphoryl center yielding products formed exclusively by the desulfurization pathway.

In the reaction between *tert*-butylphenyloxophosphoranesulfenyl chloride (**2c**) and **3f**, the primary phosphonium salt **18** does not decompose into desulfurization products because of the steric hindrance at the phosphoryl center. Therefore, formation of the isomeric salt **20** (via steps b and c) is favored. The salt **20** finally decomposes into deoxygenation products (step d). The last step of this reaction determines the rate of this process.

## Conclusion

It was shown, by low-temperature $^{31}P$ NMR studies, that interaction between **2** and tricoordinate phosphorus compounds **3** invariably results in formation of the primary phosphonium intermediate containing a sulfur bridge $>P(O)—S—\overset{+}{P}< Cl^-$. The NMR experiments confirmed the observed stereochemistry. This key intermediate has electrophilic centers at phosphoryl and phosphonium phosphorus atoms and also at carbon or silicon atoms, when alkoxy or silyloxy ligands are present. The rate of nucleophilic attack of the chlorine counterion on any particular center depends on the electronic and steric factors of the substituent around the phosphorus and reaction conditions. With the knowledge of that, the reactions of sulfenyl chlorides **2** with $P^{III}$ compounds **3** can be controlled in a selective manner.

Selective attack of the chloride counterion on the phosphoryl center (path a, Scheme I) is involved in the desulfurization pathway, while selective attack of the chloride anion on the phosphonium center (path b, Scheme I) leads to deoxygenation via the second phosphonium intermediate with an oxygen bridge $>P(S)—O—\overset{+}{P}< Cl^-$. It is likely that the pentacoordinate species are a transient intermediates in the formation of the phosphonium salts. An experimental study of this problem is currently underway.

Our results give no support to the hypothesis suggested by other authors[22] that "positive chloride" of sulfenyl chlorides attacks the $P^{III}$ center.

## Experimental Section

Boiling points were uncorrected. Solvents and commercial reagents were purified by conventional methods. Products were identified with $^{31}P$ NMR. Optical rotation measurements were made with a Perkin-Elmer 141 photopolarimeter (sensitivity = 0.002°). $^{31}P$ NMR spectra were recorded on a FT JEOL FX-60H spectrometer at 24.3 MHz and on a FT Bruker HX-72 spectrometer at 36 MHz. Positive NMR chemical shifts were reported in parts per million (ppm) downfield from 85% $H_3PO_4$ as external standard. Variable-temperature spectra were monitored usually at 10 °C and 10-min intervals and were recorded on solutions containing the compounds (0.5–1 mmol) in methylene chloride (2.5 mL). Ethyl chloride was used as a solvent for the lowest temperatures.

**Materials. Trineopentyl phosphite (3a),[23] tris(dimethylamino)phosphine (3c),[23] tris(diethylamino)phosphine (3d),[25] di-*tert*-butylchlorophosphine (3e),[24] *trans*-2-phenoxy-4-methyl-1,3,2-dioxaphosphorinane (3h),[26] *cis*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (3i),[18] *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (3j)[18] and *trans*-2-chloro-4-methyl-1,3,2-dioxaphosphorinane (3k)[27]** were prepared by conventional methods.

**Diethoxyoxophosphoranesulfenyl chloride (2a),[7] 2-(chlorothio)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (2d),[28] *cis*-2-(chlorothio)-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (2f),[20] and *trans*-2-(chlorothio)-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (2g)[20]** were synthesized by treating corresponding triethylphosphorothioate, *cis*- and *trans*-2-methoxy-2-thiono-4-methyl-1,3,2-dioxaphosphorinanes,[18] and 2-[(trimethylsilyl)oxy]-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane[28] with an equimolar amount of sulfuryl chloride according to the method of Michalski, Skowrońska et al.[7,20,28]

**(Ethyloxy)ethyloxophosphoranesulfenyl chloride (2b),** $\delta^{31}P$ 60.2 ppm, was prepared by the chlorination of *O*-ethyltrimethylsilyl ethylphosphorothioate with sulfuryl chloride according to Skowrońska et al.[28]

***tert*-Butylphenyloxophosphoranesulfenyl chloride (2c),** $\delta^{31}P$ 67 ppm, was obtained from the reaction of *tert*-butyl-

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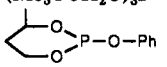
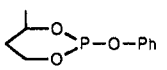
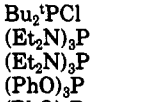
(23) Houben-Weyl, *Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1963; Vol. XII/2, pp 53, 108.
(24) Veskuil, W.; Arens, J. F. *Rec. Trav. Chim.* **1963**, *82*, 302.
(25) (a) Zwierzak, A. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1965**, *13*, 609. (b) Stuebe, S.; Lankelmov, H. P. *J. Am. Chem. Soc.* **1956**, *78*, 976.
(26) Nifant'ev, E. E.; Fursenko, J. V. *Zh. Obshch. Khim.* **1968**, *38*, 1295.
(27) (a) Zwierzak, A. *Can. J. Chem.* **1967**, *45*, 2501. (b) White, D. W.; Bertrand, R. O.; McEwen, G. K.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 7125.
(28) Skowrońska, A.; Dembiński, R.; Gwara, J.; Michalski, J. *Phosphorus Sulfur Relat. Elem.* **1988**, *39*, 119.

Table II. $^{31}P$ NMR Chemical Shifts of Products of the Reactions of 2 and 3

| | starting materials | | products[b] | | | |
|---|---|---|---|---|---|---|
| entry[a] | RR'P(O)Cl 2 | $R_3''P$ 3 ppm ref | RR'P(O)Cl 4 δ (ppm)[ref] | RR'P(S)Cl 5 δ (ppm)[ref] | $R_3''PS$ 6 δ (ppm)[ref] | $R_3''PO$ 7 δ (ppm)[ref] |
| 1 | $(EtO)_2P(O)Cl$ | $(Me_3CCH_3O)_3P$ | 3.5[32] | | 68.5[33] | |
| 2 | $(Et)(EtO)P(O)Cl$ | $(Me_3CCH_2O)_3P$ | 45.6[32] | | 68.0 | |
| 4 | $(EtO)_2P(O)Cl$ |  trans | 3.2 | | 54.8[16] | |
| 5 | $(Et)(EtO)P(O)Cl$ |  trans | 45.0 | | 54.8 | |
| 8 | $(EtO)_2P(O)Cl$ | $Bu_2^tPCl$ | 3.6 | 147.5 | | |
| 9 | $(EtO)_2P(O)Cl$ | $(Et_2N)_3P$ | 3.5 | | 78.0[33] | |
| 10 | $(Et)(EtO)P(O)Cl$ | $(Et_2N)_3P$ | 45.0 | 106.2[32] | 79.0 | 24.0[33] |
| 12 | $(Et)(EtO)P(O)Cl$ | $(PhO)_3P$ | 44.1 | 107.0 | 53.4[33] | -17.3[32] |
| 13 | $(EtO)_2P(O)Cl$ | $(PhO)_3P$ | 3.5 | 68.0[4c] | 53.6 | -18.0 |
| 15 |  | $PCl_3$ | -2.5[4c] | 58.0[4c] | 29.3 | 3.2 |
| 16 | $(Et)(EtO)P(O)Cl$ | $Ph_3P$ | 45.0 | 107.7 | 42.3[34] | 25.0[34] |
| 18 | $(EtO)_2P(O)Cl$ | $Ph_3P$ | 3.5 | 67.8 | 42.0 | 27.5 |
| 19 | $(EtO)_2P(O)Cl$ | $PCl_3$ | 3.2 | 68.0 | 28.0 | 3.8 |
| 20 | $Bu^tPhP(O)Cl$ | $Ph_3P$ | | 114.0[35] | | 27.0 |

[a] The entries are in the same order as in Table I. [b] No other products except from shown here were detected in $^{31}P$ NMR.

phenylphosphinothioic acid[29] with sulfuryl chloride as described by Michalski et al.[30]

**(Ethyloxy)ethylphosphonothioic acid (21),** bp 67–68 °C (0.2 mmHg), $n^{23}_D$ 1.4886, was obtained and resolved into optical antipodes as described by Aaron et al.[31]

**Reactions of Oxophosphoranesulfenyl Chloride (2) with Tricoordinate Phosphorus Compounds 3. General Procedure.** To a solution of sulfenyl chloride **2**, (0.02 mol) in methylene chloride (30 mL) was added dropwise a solution of **3**, (0.02 mol) in $CH_2Cl_2$ (25 mL) with stirring under a dry argon atmosphere. The temperature of the reaction mixture was kept at -20 °C. Stirring was continued at room temperature for 10 min. The solvent was evaporated, and the crude reaction mixture was analyzed by $^{31}P$ NMR spectroscopy. The proportion of the products formed are collected in Table I, and their $^{31}P$ NMR data are given in Table II and in Schemes II and III.

**Diethoxyoxophosphoranesulfenyl Chloride (2a) with Triphenylphosphine (3f) at (a) -20 °C and (b) -100 °C.** (a) From **2a** and **3f** triphenylphosphine sulfide[34] **(6f)** ($\delta^{31}P$ 42 ppm, 5%), *O,O*-diethyl phosphorochloridate[32] **(4a)**, ($\delta^{31}P$ 3.5 ppm, 5%) together with triphenylphosphine oxide[34] **(7f)** ($\delta^{31}P$ 27.5 ppm, 45%), and *O,O*-diethyl phosphorochloridothioate[4c] **(5a)** ($\delta^{31}P$ 67.8 ppm, 45%) were obtained. (b) The analogous reaction of **2a** with **3f** was carried out in ethyl chloride at -100 °C. The reaction mixture was kept at that temperature for 1.5 h and was found ($^{31}P$ NMR, -80 °C) to contain pure phosphonium salt **11f** (δ 59.5 ppm, 54.3 ppm, $^2J_{PP}$ 33.2 Hz, 100%). After the temperature was raised to 20 °C, the $^{31}P$ NMR spectrum recorded at ambient temperature showed the formation of triphenylphosphine oxide **(7f)** (δ 28 ppm, 50%) and *O,O*-diethyl phosphorochloridothioate **(5a)** (δ 68.1 ppm, 50%).

**Bis(diethoxyphosphoryl) Disulfide (1a) with Triphenylphosphine (3f) in the Presence of Chlorotriphenylphosphonium Chloride (13).** To a solution of **1a** and **3f** in ethyl chloride, mixed at -100 °C, was added a solution of **13** in $CH_2Cl_2$ at -90 °C. The resulting reaction mixture was stirred for 1.5 h at -50 °C and after the temperature was raised to 20 °C was found by means of $^{31}P$ NMR to contain 10% of *O,O*-diethyl phosphorochloridate **(4a)** (δ 3.5 ppm), 11.7% of triphenylphosphine sulfide **(6f)** (δ 42.3 ppm), 38.3% of *O,O*-diethyl phosphorochloridothioate **(5a)** (δ 68 ppm), and 40% of triphenylphosphine oxide **(7f)** (δ 27.1 ppm).

**Bis(diethoxyphosphoryl) Disulfide (1a) with Triphenylphosphine (3f) in the Presence of Boron Trifluoride Etherate.** To a solution of **1a** (0.338 g, 0.001 mol) and boron trifluoride etherate (0.284 g, 0.002 mol) in ethyl chloride (2 mL) was added a solution of **3f** (0.262 g, 0.001 mol) in EtCl (2 mL) at -100 °C. The resulting reaction mixture was mixed at the same temperature (-100 °C, 1 h). The $^{31}P$ NMR spectrum recorded at -90 °C revealed the presence of pure phosphonium salt **16** (δ 42.6 ppm, 6.8 ppm, $^2J_{PP}$ 11.8 Hz, 100%).

**Reaction of Optically Active (Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Tricoordinate Phosphorus Compounds. (Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Triphenyl Phosphite (3b).** To a solution of *O*-ethyl ethylphosphonothioic acid (21) [3.08 g, 0.02 mol, $[\alpha]^{20}_D$ +12.91° (neat)] in methylene chloride (40 mL) was added dropwise a solution of sulfuryl chloride (2.7 g, 0.02 mol) in $CH_2Cl_2$ (20 mL) at -40 °C with stirring under a dry argon atmosphere. Stirring was continued at -15 °C for 10 min. The solvent and volatile products were removed under reduced pressure at -10 °C, and crude **2b** was dissolved in benzene/*n*-hexane (1:1, 30 mL). The solution was cooled to -20 °C, and **3b** (16.2 g, 0.02 mol) in benzene/*n*-hexane (30 mL) was added dropwise. The mixture was stirred at -20 °C for 10 min, and the solvent was removed under vacuum. $^{31}P$ NMR analysis of the reaction mixture revealed the presence of *O*-ethyl phosphorochloridate **(4b)** (δ 44.1 ppm, 46%), *O,O,O*-triphenyl phosphorothionate **(6b)** (δ 53.4 ppm, 46%), and *O*-ethyl ethylphosphorochloridothioate **(5b)** (δ 107 ppm, 4%) and triphenyl phosphate **(7b)** (δ -17.3 ppm, 4%). High vacuum distillation afforded the fraction [bp 20–23 °C (0.05 mmHg), $[\alpha]^{20}_D$ -54.4° (neat)] which was found to contain **4b** (δ 45.1 ppm, 96%) and **5b** (δ 107 ppm, 4%). The optically active chloride **4b** racemizes readily and a separation requires as low a temperature as possible.[36] The initial rotation value $[\alpha]^{20}_D$ -54.4° (neat) changed after 48 h to $[\alpha]^{20}_D$ +0.81° (neat). This fraction was hydrolyzed with aqueous $K_2CO_3$ (10%), 50 mL), extracted with benzene (4 × 25 mL), and dried over anhydrous $MgSO_4$. Evaporation followed by the high-vacuum distillation afforded pure *O*-ethyl

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(31) Aaron, H. S.; Shryne, T. M.; Miller, J. J. *J. Am. Chem. Soc.* **1958**, *80*, 107.
(32) Mark, N.; Van Wazer, J. R. *Topics in Phosphorus Chemistry*; J. Wiley and Sons: New York, 1967; Vol. VB.
(33) Mavell, G. In *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London and New York, 1973.
(34) Kossolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; J. Wiley and Sons: New York, 1972; Vol. III, p 431; Vol. IV, p 32.
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ethylphosphorochloridothioate (**5b**) [0.24 g, bp 24-25 °C (0.3 mmHg), $n^{20}_D$ 1.4885, $[\alpha]^{20}_D$ +52.35° (benzene)].[37]

**(Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Triphenylphosphine (3f).** According to the procedure described above from **2b** (3.77 g, 0.02 mol) and **3f** (4.6 g, 0.02 mol) a mixture of **4b** ($\delta^{31}$P 45 ppm, 30%), **5b** ($\delta^{31}$P 107.7 ppm, 20%), **6f** ($\delta^{31}$P 42.3 ppm, 30%), and **7f** ($\delta^{31}$P 25.5 ppm, 20%) was obtained. The fraction containing **4b** ($\delta$ 46.5 ppm, 60%) and **5b** ($\delta$ 106 ppm, 40%) was obtained after high-vacuum distillation [bp 21-23 °C (0.05 mmHg), $n^{20}_D$ 1.4580, $[\alpha]^{20}_D$ -12.9° (neat)]. This rotation value was changed after 21 h to $[\alpha]^{20}_D$ +23.4° (neat). This fraction was hydrolyzed by standard methods to yield **5b** [bp 23-24 °C (0.2 mmHg), $n^{20}_D$ 11.4880, $\delta$ $^{31}$P 106.5 ppm, $[\alpha]^{20}_D$ +52.0° (neat)].

**(Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Tris(diethylamino)phosphine (3d).** The same procedure was applied to the reaction of **2b** (3.77 g, 0.02 mol) and **3d** (4.04 g, 0.02 mol). $^{31}$P NMR analysis of crude reaction mixture, $[\alpha]^{20}_D$ +0.96° (neat), revealed the presence of **4b** ($\delta$ 45 ppm, 48%), **5b** ($\delta$ 106.2 ppm, 2%), hexaethyloamide of thiophosphoric acid (**6d**) ($\delta$ 79 ppm, 47%), and tris(diethylamino)phosphine oxide (**7d**) ($\delta$ 24 ppm, 3%). High-vacuum distillation afforded the fraction [1.5 g, bp 20-22 °C (0.05 mmHg), $[\alpha]^{22}_D$ +0.04° (neat)] which was found to contain **4b** ($\delta$ 45.2 ppm, 100%). The rotation value of this fraction changed after 40 min to $[\alpha]^{20}_D$ -0.07° (neat).

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# Hydroboration. 88. Borane-1,4-Thioxane. A New, Convenient Hydroborating Agent for the Preparation of Representative Borane Reagents

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Borane-1,4-thioxane (BOT) (**1**), readily synthesized by adding diborane to 1,4-thioxane (**2**), is a stable liquid at 25 °C, which crystallizes on cooling to 0 °C, mp 11-15 °C. The neat reagent is 8.0 M in borane. It hydroborates alkenes rapidly in 3:1 mole ratio to form the corresponding trialkylborane in excellent yield. By varying the stoichiometric ratio of alkenes to 1 to 1:1 and 2:1 molar ratios, in certain cases monoalkylboranes, such as thexylborane (**7**) and monoisopinocampheylborane (**8**), and dialkylboranes, such as disiamylborane (**3**), dicyclohexylborane (**4**), diisopinocampheylborane (**6**), and 9-borabicyclo[3.3.1]nonane (9-BBN) (**5**), could be synthesized. The hydroboration reaction can be carried out at 25 °C in a wide variety of solvents, such as tetrahydrofuran (THF), diethyl ether (EE), methylene chloride ($CH_2Cl_2$), and pentane, or with neat reagents at 0 and 25 °C. It has been demonstrated that the presence of **2** does not interfere with the subsequent in situ utilization of these substituted borane reagents for further transformations. Unlike the ligand methyl sulfide, which is completely insoluble in water, **2** is moderately soluble in water (0.3 M). Consequently, it can be washed out with water from solutions in EE, $CH_2Cl_2$, and pentane. Therefore, the organoborane containing **2** can be oxidized selectively to alcohol with a controlled quantity of hydrogen peroxide in the presence of excess sodium hydroxide without attack on **2**. **2** in turn can then be removed by washing with water. Alternatively, **2** can be oxidized selectively in the presence of the organoborane by aqueous sodium hypochlorite. The resulting sulfoxide is highly soluble in water and is readily washed away from the organoboranes, thus enabling the organoboranes to be utilized for the many transformations it undergoes. In the case of stable and isolable reagents, such as 9-BBN, **2** can be removed either by decantation along with the solvent or by distillation during neat reaction. The two asymmetric hydroborating agents **8** and **6** were utilized for asymmetric syntheses by the hydroboration-oxidation reaction of 1-methyl-1-cyclopentene and *cis*-2-butene, respectively, to yield *trans*-2-methylcyclopentanol and 2-butanol in 73% and 97% ee.

The applicability of borane-tetrahydrofuran[2] ($BH_3$·THF) and borane-methyl sulfide[3] (BMS) as valuable hydroborating agents is well recognized. Thus, $BH_3$·THF and BMS hydroborate essentially all alkenes rapidly and quantitatively to yield a wide variety of fully or partially substituted organoboranes. While the application of the commercially available dilute solution of borane in THF (1 M)[4] essentially limits its applicability to THF as solvent, BMS (10 M in $BH_3$) can be utilized in a wide variety of solvents.[3] Moreover, BMS is stable at room temperature for long periods of time, whereas $BH_3$·THF undergoes a slow, but significant, cleavage of THF at room temperature, with loss of hydride.[5]

These advantages of BMS are sometimes negated by the properties of the ligand, dimethyl sulfide, present in the reaction mixture. It is insoluble in water and cannot therefore be removed from the reaction products by washing with water. It is highly volatile and odoriferous, and often draws complaints and criticisms from users of BMS or their neighbors. (On the other hand, it can be considered an excellent warning agent of poor experimental techniques.[6])

The readily available 1,4-thioxane (**2**) possesses a lower vapor pressure and a less obnoxious odor than methyl sulfide. It has the additional advantage that it is mod-

(1) Postdoctoral research associate on Grant 2 RO1 GM 10937-14 from the National Institutes of Health.

(2) Brown, H. C. Hydroboration; W. A. Benjamin: New York, 1962.

(3) (a) Braun, L. M.; Braun, R. A.; Crissman, H. R.; Opperman, M.; Adams, R. M. *J. Org. Chem.* **1971**, *36*, 2388. (b) Lane, C. F. *Ibid.* **1974**, *39*, 1437. (c) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *Ibid.* **1977**, *42*, 1392.

(4) Available from Aldrich Chemical Co.

(5) Kollonitsch, J. *J. Am. Chem. Soc.* **1961**, *83*, 1515.

(6) See Chapter 9 of ref 17 for a review of techniques.

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