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Chemistry of Thiono- and Selenonophosphoranes. A Mechanistic Study of Chlorination Reactions of Phosphorus Thionoesters >P(S)OR: Reactive Intermediates and Stereochemistry[1]

Jan Michalski,* Jerzy Mikołajczak, and Aleksandra Skowrońska*

Contribution from the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna 5, 90-362 Łódź, Poland. *Received August 12, 1977*

Abstract: Low-temperature ^{31}P NMR spectroscopy and stereochemical data obtained from compounds having optically active phosphorus and carbon centers have been applied to elucidate the mechanism of the reaction between phosphorus thionoesters >P(S)OR (**1**) and chlorine or sulfuryl chloride. Phosphonium intermediates were unambiguously detected and depending on the substituent at the phosphorus atom may or may not undergo nucleophilic displacement of ligands. Chloridates >P(O)Cl (**4**), elemental sulfur, and alkyl halides are formed in the first case and oxophosphoranesulfenyl chlorides >P(O)SCl (**3**) and alkyl halides in the latter. The structures of the phosphonium intermediates were confirmed through independent synthesis by Arbuzov-type reactions.

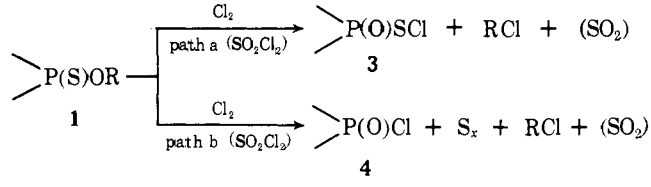
Two series of esters of phosphorus monothio acids are known: thionates **1** and thiolates **2.** Among the chemical transformations of esters **1** and **2** reactions with halogens and sulfuryl chloride are of special interest. Saville[2] and Stirling[3] were the first to describe the reaction of **2** with halogens. It has been demonstrated in this laboratory that this reaction is of general importance and can be widely employed for synthetic and stereochemical purposes.[4]

$$>P(O)SR \xrightarrow{X_2} >P(O)X + XSR$$

2

The reaction of trialkylphosphorothionates $(RO)_3P{=}S$ with chlorinating agents such as elemental chlorine or sulfuryl chloride has been reported by Michalski and Skowrońska and explored as a general route to compounds containing the >P(O)SCl (**3**) functional group.[5] We have examined the influence of the environment at the phosphorus atom on the reaction of thionoesters **1** with elemental chlorine and sulfuryl chloride. We have found that depending on the structure of **1** reaction with a chlorinating agent can proceed either predominantly via path a with the formation of oxophosphoranesulfenyl chloride (**3**) and alkyl chloride or via path b with the formation of chloridate **4,** elemental sulfur, and alkyl chloride. Acyclic phosphorothionates and six-membered cyclic thionates are chlorinated exclusively with release of alkyl chlorides and formation of oxophosphoranesulfenyl chlorides **3.** In contrast, acyclic phosphono- and phosphinothionates, as well as some other types of thionates **1,** release alkyl chloride and elemental sulfur with the formation of the corresponding chloridates **4.** Cases in which both paths a and b are followed were also encountered. We report a detailed study of these reactions and propose a general mechanistic scheme based both on intermediates detected by low-temperature ^{31}P NMR spectroscopy and on stereochemical changes observed.

Scheme I



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Scheme II

$(RO)_3P{=}S$ (**5**) $\xrightarrow[\text{or } SO_2Cl_2]{Cl_2}$ $[(RO)_3\overset{+}{P}{-}SCl\ \overset{-}{Cl}]$ (**6**)

^{31}P **a**, δ −66.5 ppm; b, δ −67.5 ppm

^{31}P **a**, δ −45 ppm; b, δ −43.6 ppm

$\xrightarrow[-SO_2]{-RCl}$ $(RO)_2P(O)SCl$ (**7**)

^{31}P **a**, δ −19 ppm; b, δ −18.2 ppm

a, R = Et; **b**, R = *n*-Bu

Results and Discussion

Chlorination of Organyl Phosphorothionates. Phosphorus thionoesters **1** react with elemental chlorine or sulfuryl chloride below ambient temperature. For example, phosphorothionates **5** (Scheme II) react readily at −70 °C and phosphonothionates **11** (Scheme IV) even at −90 °C. In liquid nitrogen no detectable reaction takes place making it possible to keep the substrates together unreacted. In a typical experiment trialkylphosphorothionate **5** was dissolved in methylene chloride or ethyl chloride. After the solution was cooled in liquid nitrogen an equimolar quantity of the chlorinating agent was added. When the temperature had risen to −70 °C the ^{31}P NMR spectrum and the independent synthesis described below clearly indicated formation of the phosphonium salt **6**. At −30 °C fast conversion of the phosphonium salt **6** into oxophosphoranesulfenyl chloride **7** and alkyl halide was observed. The reactions presented in Scheme II are clear cut and no other products containing phosphorus were observed by ^{31}P NMR spectroscopy (Figure 1). The spectral properties of **6a** and **6b** are identical with those of compounds prepared via the Arbuzov reaction of trialkyl phosphites with sulfur dichloride:

$(RO)_3P + SCl_2 \xrightarrow{-70\ °C} [(RO)_3\overset{+}{P}\text{-}SCl\ \overset{-}{Cl}]$ ^{31}P

9 **6**

a, δ − 45.5 ppm

b, δ − 44 ppm

Although the phosphonium salts **6** were in this case the major products, small quantities of the chlorophosphonium salts **8** have also been observed which are most likely derived from the elemental chlorine present in the system:

$$2SCl_2 \rightleftarrows Cl_2 + S_2Cl_2$$

The salt **8** could also be prepared directly from trialkyl phosphite **9** and elemental chlorine in ethyl chloride solution at −80 °C:

$(RO)_3P + Cl_2 \rightarrow [(RO)_3\overset{+}{P}\text{-}Cl\ \overset{-}{Cl}] \rightarrow (RO)_2P(O)Cl + RCl$

9 **8** **10**

^{31}P **8a**, δ − 16.2 ppm

b, δ − 16.7 ppm

The thermal stability of **8** was distinctly lower than that of **6** and even at −50 °C **8** decomposes into the chloridate **10** via nucleophilic displacement at carbon in a manner typical for the dealkylation step of the Arbuzov reaction. The overall process leading to **10** is well known in synthetic organophosphorus chemistry.[26]

Formation of the phosphonium intermediates **6c** and **6d** was also demonstrated by ^{31}P NMR spectroscopy and correlated with the stereochemical changes observed at the phosphorus atom in the case of diastereoisomeric six-membered phosphorothionates: 2-methoxy-2-thiono-4-methyl-1,3,2-dioxaphosphorinans *cis*-**5c** and *trans*-**5d**. In a procedure similar to that described above for **5a** and **5b** after warming the reagents from liquid nitrogen temperature to −70 °C, diastereoisomeric phosphonium salts **6c** and **6d** were readily evident from their

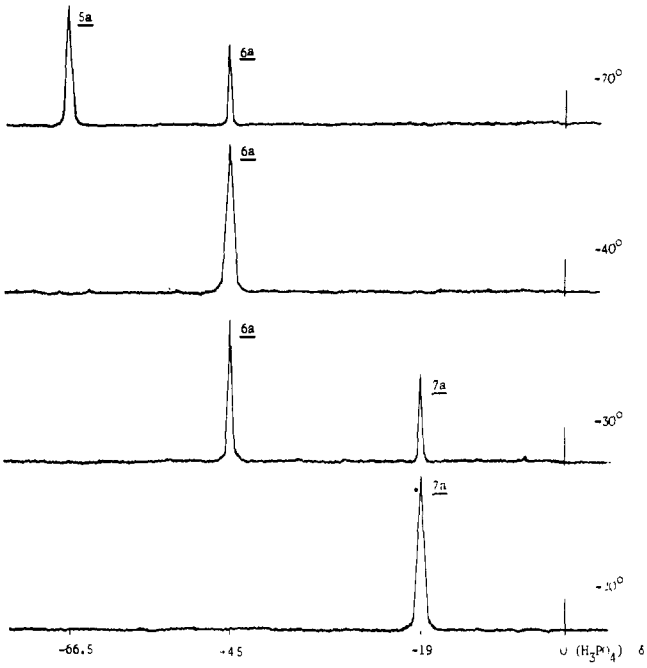
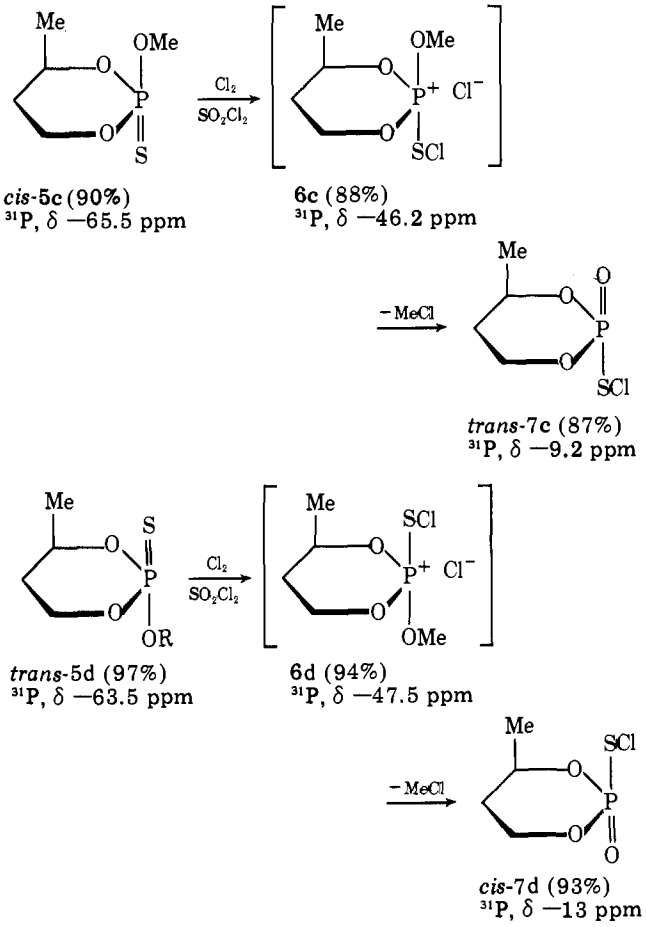


Figure 1. The proton-decoupled ^{31}P NMR spectra of a mixture of triethylphosphorothionate **5a** (0.5 mmol) and chlorine (0.5 mmol) in methylene chloride at different temperatures.

^{31}P NMR spectra. The subsequent dealkylation is complete at −30 °C. The stereochemical configurations of **5c** and **5d** were determined previously.[6] Stereochemical assignments for sulfenyl chlorides **7c** and **7d** have recently been established in this laboratory.[7]

The chlorination reactions described in Scheme III are

Scheme III



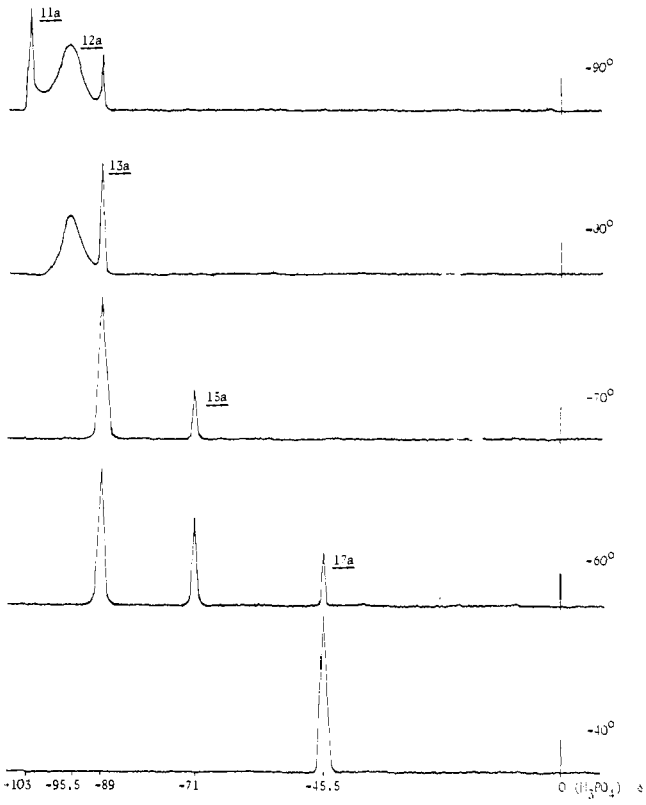


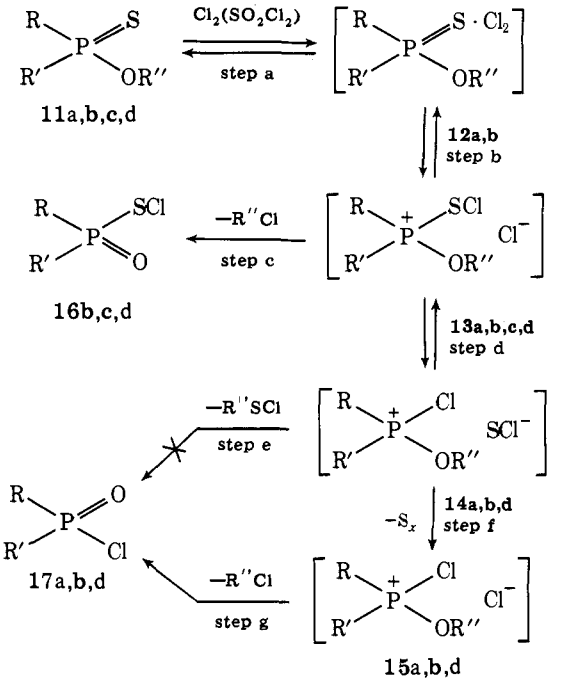
Figure 2. The proton-decoupled ^{31}P NMR spectra of a mixture of *O*-diethyl ethylphosphonothionate (**11a**, 0.7 mmol) with chlorine (0.7 mmol) in ethyl chloride at different temperatures.

stereospecific and proceed with full retention of configuration at the phosphorus atom. Excellent, nearly quantitative yields of the oxophosphoranesulfenyl chlorides **7** and **16c** of high purity are obtained in chlorination of the corresponding thionoesters **5** and **11c**, provided that all operations, including the removal of solvent, are performed in a moisture-free atmosphere of an inert gas. Although sulfenyl chlorides of type **7** are volatile enough to be distilled in vacuo, this procedure is invariably accompanied by some decomposition.

Chlorination of Organyl Phosphono- and Phosphinothionates. The nature of the reaction between chlorine or sulfuryl chloride and thionoesters containing a direct phosphorus–carbon bond is also clear in spite of its greater complexity. Chlorination of **11a** at −90 °C resulted in the formation of a complex **12a** (step a, Scheme IV) with a $\delta^{31}P$ value close to that of the thionoester **11a**. It is, however, premature to draw any definite conclusion concerning the structure of **12a** on the basis of the ^{31}P NMR spectrum. After the reaction mixture was warmed to −70 °C the phosphonium complex **13a,b,d** appeared (step b), accompanied by a second phosphonium complex **14a,b,d** formed in step d. When the reaction mixture was allowed to warm to −50 °C for several minutes a chloridate **17a,b,d**, elemental sulfur, and an alkyl halide were formed in the irreversible step f. The chemical changes described above are depicted in Figure 2. All of the experimental facts presented above can be readily accommodated as outlined in Scheme IV. It is interesting to note that we were never able to detect any alkanesulfenyl chloride which would involve step e. The most important step is the nucleophilic ligand exchange (step d) leading to an equilibrium between phosphonium salts **13** and **14**.

The process of ligand exchange (step d) is in accord with the greater electrophilicity of the phosphorus center in **13a,b,d** in comparison with **6a,b** and **6c,d**. This ligand exchange must be faster than dealkylation of **13a,b,d** which leads to **16** (step c).

Scheme IV



a, R = Et; R′ = OEt; R″ = Et
c, R = Bu-*t*; R′ = OEt; R″ = Et
b, R = Ph; R′ = OBu; R″ = Bu
d, R = R′ = R″ = Me

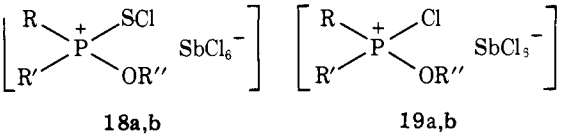
^{31}P NMR chemical shifts, δ ppm

	11	12	13	15	16	17	18	19
a	−103	−94.5	−89	−71		−45.5	−89.5	−70
b	−101	−93	−73	−55	−41	−29	−73.5	−54
c	−107.3		−97		−62.7			
d	−94.5		−113	−77	−68.7	−60.3		

Transformation of the phosphonium salts **14** into **15** is due to the fragmentation of the thermodynamically unstable anion SCl^- into chloride ion and elemental sulfur:

$$x(^-S\text{-}Cl) \rightarrow S_x + xCl^-$$

This picture is supported by the fact that it has been possible to transform both phosphonium salts **13a,b** and **15a,b** (before and after ligand exchange) into relatively stable antimonates **18a,b** and **19a,b** by treating the reaction mixture with a small

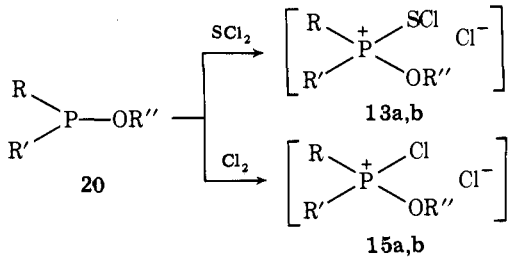


18a,b **19a,b**

^{31}P **18a**, δ −89.5 ppm
18b, δ −73.5 ppm
19a, δ −70.0 ppm
19b, δ −54.0 ppm

excess of antimonium pentachloride. The phosphonium hexachloroantimonates **18** and **19** are stable at ambient temperatures owing to the low C nucleophilicity of the counteranion.

Furthermore, **13a,b** and **15a,b** can be synthesized independently by the Arbuzov reaction between corresponding phosphonites **20** and sulfur dichloride or chlorine. The salts **13** and **15** were prepared by mixing the reagents in ethyl chloride solution at the temperature of liquid nitrogen and allowing the solution to warm gradually to −40 °C. Conversion of **13** into **15** analogous to the reactions previously described involving the chlorination of **11** was also observed in the temperature range between −80 and −40 °C.



^{31}P 13a, δ −88.5 ppm
13b, δ −72.5 ppm
15a, δ −70.3 ppm
15b, δ −54.5 ppm

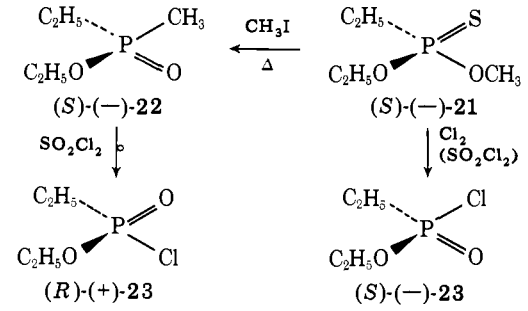
The ^{31}P chemical shifts of phosphonium salts **13, 15** and **18, 19** are very close. This suggests that compounds **13** and **15** have "true" phosphonium structure with little interaction within the ion pair involved. Introduction of steric hindrance should change the reaction course toward step c leading to oxophosphoranesulfenyl chloride. Indeed, chlorination of ester **11c** containing a *tert*-butyl group attached directly to the phosphorus atom gave **16c** in excellent yield. Ligand exchange must in this case be very slow because of the pronounced influence of the steric hindrance on the rate of nucleophilic displacement at a phosphorus center.[8]

Stereochemistry. Ligand exchange should also result in definite stereochemical changes when optically active thionoester is used. Indeed optically active *O*-ethyl-*O*-methyl ethylphosphonothioate (**21,** $[\alpha]_{578}$ − 2.25°) was converted into *O*-ethyl ethylphosphonochloridate (**23,** $[\alpha]_{578}$ − 15.05°) with inversion of configuration at the phosphorus atom. The stereochemical course of this reaction has been elucidated by employing a reaction of known stereochemistry. (*S*)-(−)-*O*-ethyl-*S*-methyl ethylphosphonothiolate (**22**) was obtained by alkylation of (*S*)-(−)-*O*-ethyl-*O*-methyl ethylphosphonothioate (**21**). This reaction proceeds without any change of configuration. Chlorination of **21** was found to yield *O*-ethyl ethylphosphonochloridate (**23**) of a configuration opposite to that of a sample prepared from **22** by the action of sulfuryl chloride. It was demonstrated in this laboratory that the latter reaction **22** → **23** proceeds with inversion of configuration at the phosphorus atom.[9] These stereochemical relationships are summarized in Scheme V.

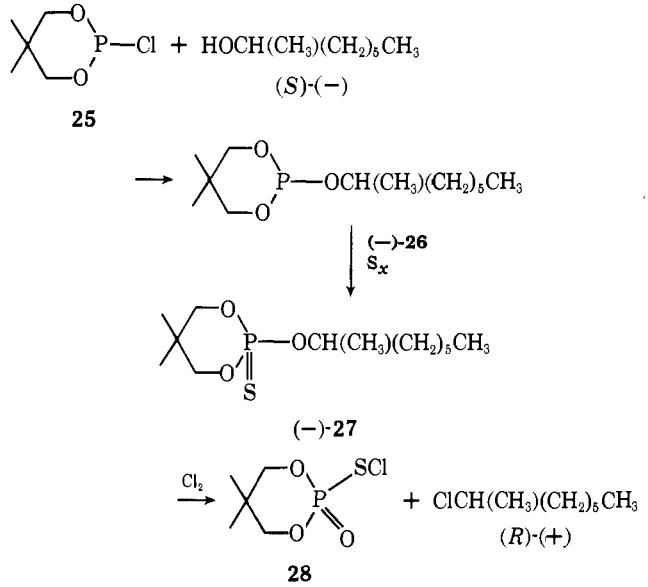
The cycle presented above constitutes, according to Cram's[10] classification, an antipodal diligostatic three-reaction cycle involving ligand methathesis which is equivalent to an additional inversion of configuration. This indicates that inversion at the phosphorus atom in the chlorination reaction of thionoester **21** must be accepted.

It was also of interest to study the product derived from the dealkylation step of the chlorination reaction in order to elucidate the mechanism involved. It is known from the work of Gerrard and Green[11] that in the Arbuzov reaction, the dealkylation step involving the phosphonium salt proceeds in agreement with an S_N2 reaction which is indicated by the inversion of configuration observed when a chiral center derived from an optically active secondary alcohol is present. The optically active phosphite **26** was synthesized from chlorophosphite **25** and (*S*)-(−)-octan-2-ol, $[\alpha]^{20}_D$ −7.54°. After addition of elemental sulfur, the thionophosphate **27** obtained was chlorinated under standard conditions to yield sulfenyl chloride **28** and (*R*)-(+)-2-chlorooctane, $[\alpha]^{20}_D$ +22.78°. From optical rotation values it is evident that the reaction is highly stereoselective and proceeds with inversion of configuration at the carbon center. The dealkylation step is therefore a simple bimolecular displacement on carbon.

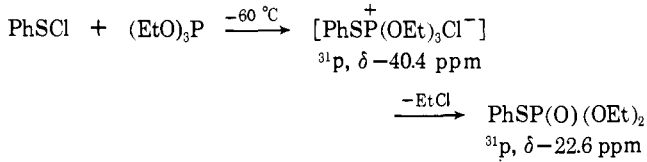
Scheme V



Scheme VI



Phosphonium Intermediates in Arbuzov Reaction. Our observation concerning Arbuzov reaction between phosphites **9,** phosphonites **20,** and elemental chlorine and sulfur dichloride described above are of some general interest. Previously phosphoniums were generally assumed to be Arbuzov intermediates[13] but only recently and then only in the case of sterically hindered phosphites have they been characterized by ^{31}P NMR spectroscopy.[14] The present work extends these observations to reactive phosphites and phosphonites in reaction with elemental chlorine or sulfur dichloride, respectively. An analogous reaction course was established for benzenesulfenyl chloride.[15]



Conclusion

The stepwise character of the chlorination of phosphorus thionoesters was established by directly detecting with ^{31}P NMR spectroscopy the phosphonium species formed in the course of ligand exchange. The substituents attached to the phosphorus atom determine the course of the reaction by promoting or hindering ligand exchange in competition with the dealkylation reaction. A ligand exchange of this type in reactions involving phosphonium intermediates has often been postulated.[12] In the present case the intermediates were directly observed and independently synthesized. It is likely that a pentacoordinate species is a transient intermediates in the formation of the phosphonium salt. An experimental study of this problem is currently underway.

Experimental Section

Solvents were purified by conventional methods. Optical activity measurements were made with a Perkin-Elmer 141 photopolarimeter.

^{31}P NMR Spectral Measurements. Variable-temperature spectra were recorded on a JEOL C-60 H spectrometer at 24.3 MHz. A heteronuclear spin decoupler INM-SD-HC was used for chemical shift determination and integration. Phosphoric acid (85%) was run prior to all samples where the chemical shift was to be determined. The sign convention used is that shifts upfield of the standard are positive, those downfield negative. Samples were prepared in methylene chloride. Ethyl chloride was used as solvent for the lowest temperatures.

I. Materials. Octan-2-ol was resolved as described.[24] **Trialkyl phosphites,**[25] ***O*-diethyl ethylphosphonite,**[16] ***O*-dibutyl phenylphosphonite,**[17] ***O*-diethyl *tert*-butylphosphonite,**[18] and ***cis*- and *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinanes**[6] were prepared by conventional methods.

Phosphorothionates, phosphonothionates, and ***cis*- and *trans*-2-methoxy-2-thiono-4-methyl-1,3,2-dioxaphosphorinanes** were obtained by addition of elemental sulfur to the corresponding trivalent phosphorus compounds at 5 °C in benzene.

***O*-Ethyl ethylphosphonothioic acid,** bp 57–50 °C (0.08 mmHg), n^{20}_D 1.4906, was obtained and resolved into optical antipodes according to Aaron et al.[19]

***O*-Ethyl ethylphosphonochloridothionate,** bp 25 °C (0.07 mmHg), n^{20}_D 1.4910, $[\alpha]^{20}_D$ −60.5° (neat), $\delta^{31}P$ −106 ppm, was obtained by treating the appropriate optically active thio acid [$[\alpha]^{20}_D$ +12.5° (neat)] with PCl_5 according to the procedure given by Michalski and Mikolajczyk.[20]

***O*-Ethyl-*O*-methyl ethylphosphonothionate (21),** bp 51 °C (5 mmHg), n^{20}_D 1.4660, $[\alpha]^{20}_D$ −2.25° (neat), $\delta^{31}P$ −102.8 ppm, was prepared by the reaction of ethyl ethylphosphonochloridothionate [$[\alpha]^{20}_D$ −60.5° (neat)] with sodium methoxide.[21]

***O*-Methyl dimethylphosphinothioate (11d)** was obtained by the reaction of methanol with an equimolar amount of dimethyl phosphinobromothioate[22] in the presence of triethylamine ($\delta^{31}P$ −94.5 ppm).

2-Octoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane (26). To a solution of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane[23] (25.3 g, 0.15 mol) and pyridine (12.65 g, 0.16 mol) in ether (300 mL), octan-2-ol (19.5 g, 0.15 mol, $[\alpha]^{20}_D$ −7.54° (neat)) in ether (150 mL) was added at −5 °C with stirring under a dry nitrogen atmosphere. Stirring was continued at room temperature for 3 h and the resulting precipitate was filtered and washed with ether. The filtrate was evaporated and the residue was distilled under reduced pressure giving **26** [bp 105–106 °C (1.3 mmHg), n^{20}_D 1.4484, $\delta^{31}P$ −134.2 ppm, $[\alpha]^{20}_D$ +14.4° (neat), yield 37 g (94%)]. Anal. Calcd for $C_{13}H_{27}O_3P$: C, 59.5; H, 10.3; P, 11.8. Found: C, 59.9; H, 10.4; P, 2.1.

2-Octoxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (27). This compound was obtained in 93% yield by addition of elemental sulfur to **26** in benzene according to the usual procedure [bp 108–110 °C (0.2 mmHg)]. The product solidified during storage at room temperature. Recrystallization from benzene–hexane gave pure **27** [mp 36–37 °C, $\delta^{31}P$ −60.3 ppm, $[\alpha]^{20}_D$ +3.2° (benzene)]. Anal. Calcd for $C_{13}H_{27}O_3PS$: C, 53.05; H, 9.2; P, 10.55. Found: C, 52.9; H, 9.1; P, 10.85.

II. Chlorination of *O*-Diethyl Ethylphosphonothionate (11a). A. With Sulfuryl Chloride. General Procedure. Freshly distilled sulfuryl chloride (2.2 g, 0.015 mol) was added dropwise with stirring to a solution of **11a** (2.75 g, 0.015 mol) in methylene chloride (20 mL). The temperature of the mixture was kept at −15 to −20 °C. Stirring was continued at room temperature for 15 min. The resulting elemental sulfur was filtered. The solvent was evaporated and the residue was distilled in vacuo giving 2.25 g (95%) of *O*-ethyl ethylphosphonochloridate [bp 34–35 °C (0.4 mmHg), $\delta^{31}P$ −46 ppm].

B. With Chlorine. The same procedure performed with **11a** and a solution of chlorine in CCl_4 yielded *O*-ethyl ethylphosphonochloridate (97% yield).

III. Chlorination of *O*-Dibutyl Phenylphosphonothionate (11b). The procedure previously described (section II) was applied to **11b** (4.3 g, 0.015 mol) using SO_2Cl_2 or Cl_2 as the reagents. ^{31}P NMR analysis of the reaction mixture (neat) revealed the presence of *P*-butoxy-*P*-phenyloxophosphoranesulfenyl chloride (20%, $\delta^{31}P$ −41 ppm) and *O*-butyl phenylphosphonochloridate (80%, $\delta^{31}P$ −29 ppm).

IV. Chlorination of *O*-Diethyl *tert*-Butylphosphonothionate (11c). The reactions of **11c** (3.9 g, 0.02 mol) with 2.7 g of SO_2Cl_2 or 1.82 g of Cl_2 (0.02 mol) were performed as described in section II. Pure *P*-ethoxy *P*-*tert*-butyloxophophoranesulfenyl chloride was isolated in 98% yield ($\delta^{31}P$ −62.7 ppm). Anal. Calcd for $C_6H_{14}O_2ClPS$: C, 33.25; H, 6.45; P, 14.3. Found: C, 32.95; H, 6.4; P, 13.85.

V. Chlorination of *O*-Methyl Dimethylphosphinothionate (11d). The procedure described (in section II) was applied to **11d. 11d** (3.75 g, 0.03 mol) with SO_2Cl_2 or Cl_2 (0.03 mol) gave a mixture of dimethyloxophosphoranesulfenyl chloride (30%, $\delta^{31}P$ −69.7 ppm) and dimethylphosphinochloridate (70%, $\delta^{31}P$ −60.3 ppm).

VI. Chlorination of Optically Active *O*-Ethyl-*O*-methyl Ethylphosphonothionate (21). Sulfuryl chloride (2.7 g, 0.02 mol) was added at −20 °C to a solution of **21** (3.35 g, 0.02 mol), $[\alpha]^{20}_D$ −2.25° (neat), in methylene chloride (15 mL). The solvent was evaporated below 10 °C. Distillation gave 2.5 g (80%) of *O*-ethyl ethylphosphonochloridate [bp 28–29 °C (0.2 mmHg), $[\alpha]^{20}_D$ −15.05° (neat)].

VII. Chlorination of 2-Octoxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (27). Sulfuryl chloride (4.05 g, 0.03 mol) was added dropwise with stirring at −10 °C to a solution of **27** in methylene chloride (20 mL). Volatile product and solvent were removed at 0.1 mmHg, trapped (−80 °C), and distilled to gave 2-chlorooctane [3.5 g (80%), n^{20}_D 1.4264, $[\alpha]^{20}_D$ +22.78°, optical purity 80%].

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