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(26) J. A. Marshall and H. Roebke, *J. Org. Chem.*, **31**, 3109 (1966). Professor Marshall kindly supplied copies of the IR and NMR spectra of their product. Comparison of these spectra with the spectra of our sample suggests that the main constituent of each sample is the same; however, the NMR spectrum of the previously described sample does have an extra small *t*-Bu peak suggesting that it may contain a small amount of a second stereoisomer.

Stereochemistry of Organophosphorus Cyclic Compounds. 6.[1] Stereochemistry of the Reaction between Sulfenyl Chlorides and Trivalent Phosphorus Compounds[2]

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cis- and *trans*-2-methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes (**3**) have been synthesized and their conformations studied by ^1H and ^{31}P NMR. *trans*-**3** is found to exist as a chair-form conformer with the ring methyl and phosphoryl group equatorial. *cis*-**3** adopts most likely a chair conformation with the ring methyl equatorial and phosphoryl group axial. It has been demonstrated that *cis*- and *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinanes (**1**) and 2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes (**2**) react with a variety of sulfenyl chlorides stereospecifically with retention at phosphorus. The same steric course has been observed for reaction between optically active *O*-isopropyl ethylphosphinate (**12**) and *O*-isopropyl *O*-trimethylsilyl ethylphosphonite (**15**) and methylsulfenyl chloride. The mechanism of reaction of trivalent phosphorus compounds with sulfenyl chlorides is discussed.

The reaction between alkyl- and arylsulfenyl chlorides and trialkyl phosphites, which takes place to give the corresponding thiophosphates and alkyl chlorides according to eq 1, was first studied by Morrison[3] in 1955.

$$(RO)_3P + R'SCl \longrightarrow (RO)_2P(=O)-SR' + RCl \qquad (1)$$

Dialkyl phosphites react analogously although in this case thiophosphate formation is accompanied by the elimination of hydrogen chloride in place of the alkyl chloride.

Reaction 1 is usually regarded as an Arbuzov-type process involving decomposition of an intermediate phosphonium chloride.[4] However, neither the mechanism nor the steric course of this reaction has been investigated in detail.[5] We were prompted to undertake a detailed study of the mechanism of reaction 1 by consideration of the fact that the phosphite molecule can attack either the sulfur or the halogen atom of the sulfenyl halide molecule. Formally, this corresponds to the two possible modes of sulfur–chlorine bond polarization.

$$R-\overset{\delta^+}{S}(Cl^{\delta^-}) \overset{1}{\leftarrow} \ddot{P}(OR)_3 \overset{2}{\rightarrow} \overset{\delta^+}{Cl}-\overset{\delta^-}{SR} \qquad (2)$$

One possible ionic mechanism consists in the nucleophilic attack of phosphite on sulfur leading to the formation of an intermediate "quasi-phosphonium salt" A (eq 3). Subsequent

$$(RO)_3P: + \overset{\delta^+}{R}\overset{\delta^-}{S}-Cl \longrightarrow \underset{A}{\left[(RO)_2\overset{+}{P}(-O-R)-SR'\ Cl^-\right]} \longrightarrow (RO)_2P(=O)-SR' + RCl \qquad (3)$$

nucleophilic attack of chloride ion on the alkoxy group yields the thiol ester and alkyl chloride. According to this mechanism formation of the thiol ester should take place with retention of configuration around the phosphorus atom.

An alternative mechanism consists in nucleophilic attack of the phosphorus atom on the "electropositive" halogen atom[6] of the sulfenyl chloride molecule leading to the formation of a chlorophosphonium salt B. Displacement of

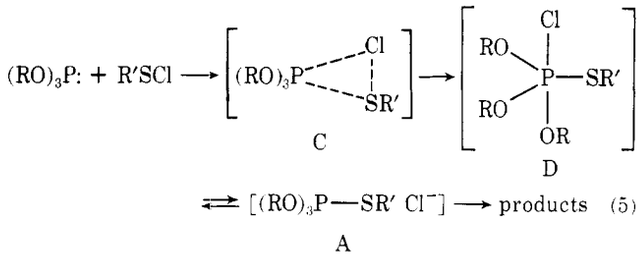
$$(RO)_3P: + \overset{\delta^+}{Cl}-\overset{\delta^-}{SR'} \longrightarrow \underset{B}{[(RO)_3\overset{+}{P}-Cl\ R'S^-]} \longrightarrow \underset{A}{\left[(RO)_2\overset{+}{P}(-O-R)-SR'\ Cl^-\right]} \longrightarrow (RO)_2P(=O)-SR' + RCl$$

$$+ (R'S)_2 + (RO)_2P(=O)-Cl \qquad (4)$$

chloride ion by attack of mercaptide ion at phosphorus would convert intermediate B to the same "quasi-phosphonium salt" A which would then undergo the normal decomposition.

The stereochemical consequence of this mechanism is that the thiol ester should have a configuration opposite to that of the initial phosphite or be formed as a racemate. Inversion of configuration around the phosphorus atom would take place during the exchange of chlorine for the thioalkyl group in the chlorophosphonium salt B whereas chloride–chloride exchange in phosphonium salt B or the mercaptide–mercaptide exchange in phosphonium salt A would be responsible for racemization.

A third mechanism involving "biphilic" addition of the trivalent phosphorus atom to the S–Cl bond might also be considered[7] (eq 5). This would lead to the formation of a

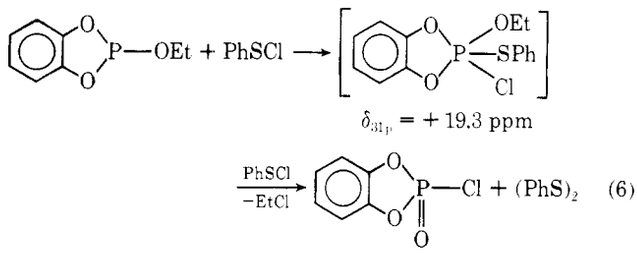


$$\rightleftharpoons [(RO)_3P{-}SR'\ Cl^-] \longrightarrow \text{products} \quad (5)$$

A

pentcovalent phosphorus intermediate D having the structure of a trigonal bipyramid in which the chlorine atom and the mercaptide group are probably situated in apical and equatorial positions, respectively. Intermediate D may be in equilibrium with the "quasi-phosphonium salt" A which then undergoes conversion to thiol ester and alkyl chloride. It should be mentioned that the pentacovalent intermediate D could be formed from either A or B. In this case the stereochemistry of the reaction would depend on the relative stability of D.[8] Rapid decomposition of D could lead to complete retention of configuration at phosphorus.

It should be emphasized that the involvement of a pentacovalent phosphorus intermediate has recently been established by Skowrońska, Mikołajczak, and Michalski[9] in the reaction between phenylsulfenyl chloride and 2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane by means of ^{31}P NMR at −80 °C.

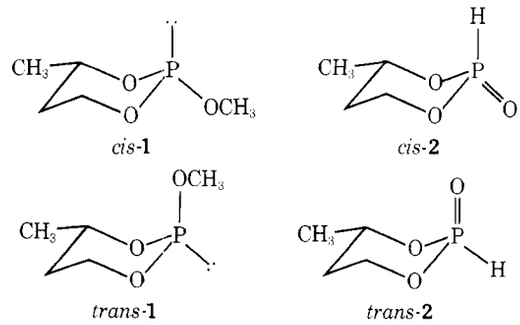


$\delta_{^{31}P} = +19.3$ ppm

(6)

The possibility of investigating the steric course of the phosphite–sulfenyl chloride reaction appeared reasonable when diastereomerically pure geometrical isomers of cyclic trivalent phosphorus compounds,[10] optically active phosphonites, R(RO)P(O)H,[11] and esters of acids containing trivalent phosphorus, RR'POR,[12] became available. Cyclic trivalent phosphorus compounds are particularly convenient as models for such studies since they are configurationally stable and the diastereomeric reaction products are readily identifiable by nuclear magnetic resonance technique.

As convenient models we have used *cis*- and *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinanes (**1**)[13,14] and *cis*- and *trans*-2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes (**2**).[14,15] The preparation and stereochemical behavior of these compounds have been described recently. In contrast to the conformationally homogeneous *trans*-**1** as well as *cis*-**2** and *trans*-**2**, the thermodynamically less stable phosphite *cis*-**1** has been shown [13]to exist as a mixture of conformers due to rapid ring flipping. However, in the conformation principally populated the ring methyl group is equatorial and this conformation is shown below.

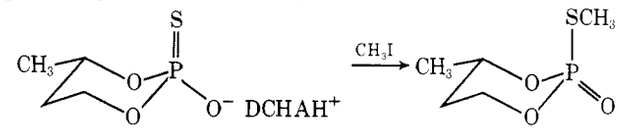


cis-**1** *cis*-**2**

trans-**1** *trans*-**2**

In order to determine the steric course of reaction 1 it was first necessary to prepare by independent, unequivocal method *cis*- and *trans*-2-thiomethyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes (**3**) which are the expected products of the reaction between the corresponding phosphites and methylsulfenyl chloride.

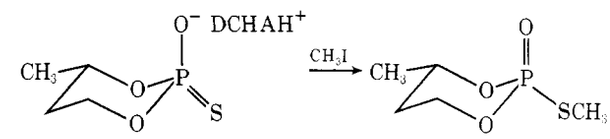
Synthesis, Configuration, and Conformation of *trans*- and *cis*-2-Methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3). Diastereomeric thiol esters **3** were obtained by methylation of the diastereomeric dicyclohexylammonium salts of 2-hydroxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (**4**) by means of methyl iodide. The configuration of *cis*- and *trans*-**4** has been previously established by Mikołajczyk and Łuczak.[14,16] Since the alkylation of thio acid salts takes place exclusively at the sulfur atom,[17] the configuration at phosphorus remains unchanged. Therefore, methylation of the trans thio acid salt gave a crystalline thio ester **3** (mp 76–78 °C) assigned the trans structure whereas the cis thio acid salt gave a liquid which was assigned the cis structure.



trans-**4**
mp 208–211 °C
$\delta_{^{31}P}$ −50.5 ppm

trans-**3**

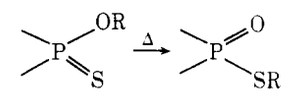
(7)



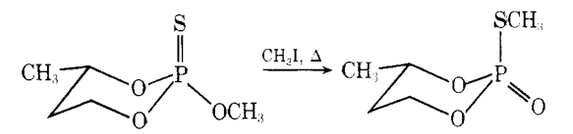
cis-**4**
mp 194–196 °C
$\delta_{^{31}P}$ −53.5 ppm

cis-**3**

Alternatively, thiol esters **3** may be prepared by the Pishschimuka reaction which involves the thermal isomerization of thionophosphates and is known to take place without configurational changes around the phosphorus atom.[18]

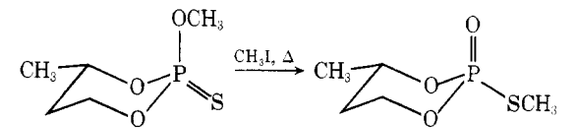


trans-2-Methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (**5**)[14,16] having a diastereomeric purity of 93% was heated with methyl iodide at 100 °C for 3 h in a sealed tube to give the same crystalline thiol ester **3** obtained from *trans*-**4**. Similarly the corresponding cis ester **5**[14,16] having a diastereomeric



trans-**5** (93% d.p.) *trans*-**3** (100% d.p.)

(8)



cis-**5** (93% d.p.) *cis*-**3** (87% d.p.)

purity of 93% gave the liquid thiol ester **3** accompanied by 13% of the isomeric *trans*-**3**. The slight decrease of diastereomeric purity in the latter reaction was probably due to the drastic reaction conditions since *cis*-**3** can suffer epimerization to the thermodynamically more stable crystalline isomer *trans*-**3**.

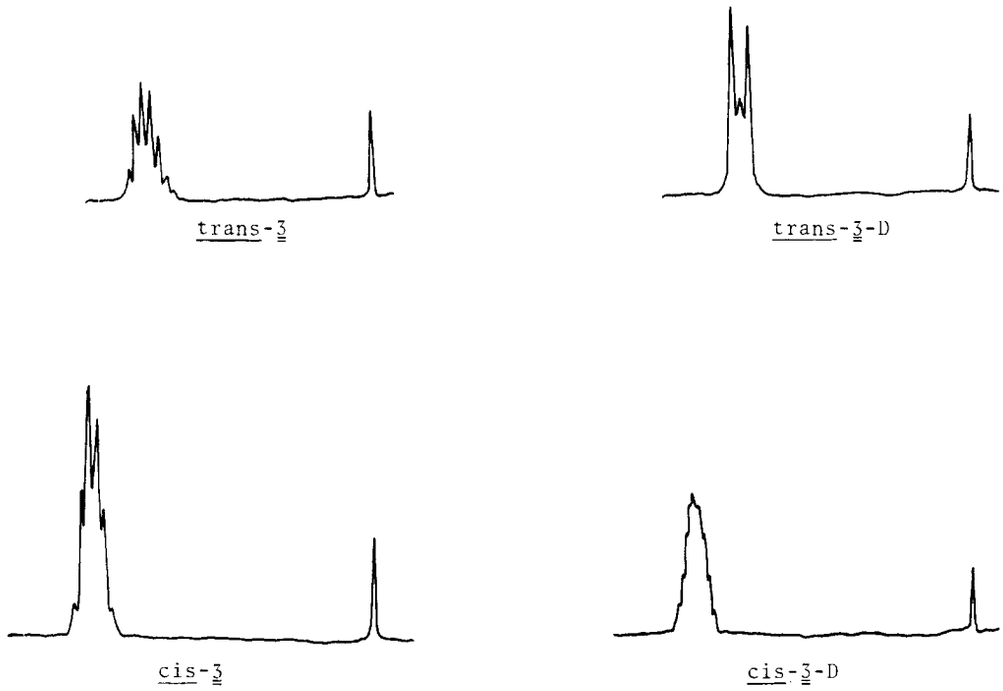


Figure 1. ^{31}P NMR spectra of *cis*- and *trans*-2-methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes (3) and their *S*-trideuteriomethyl analogues.

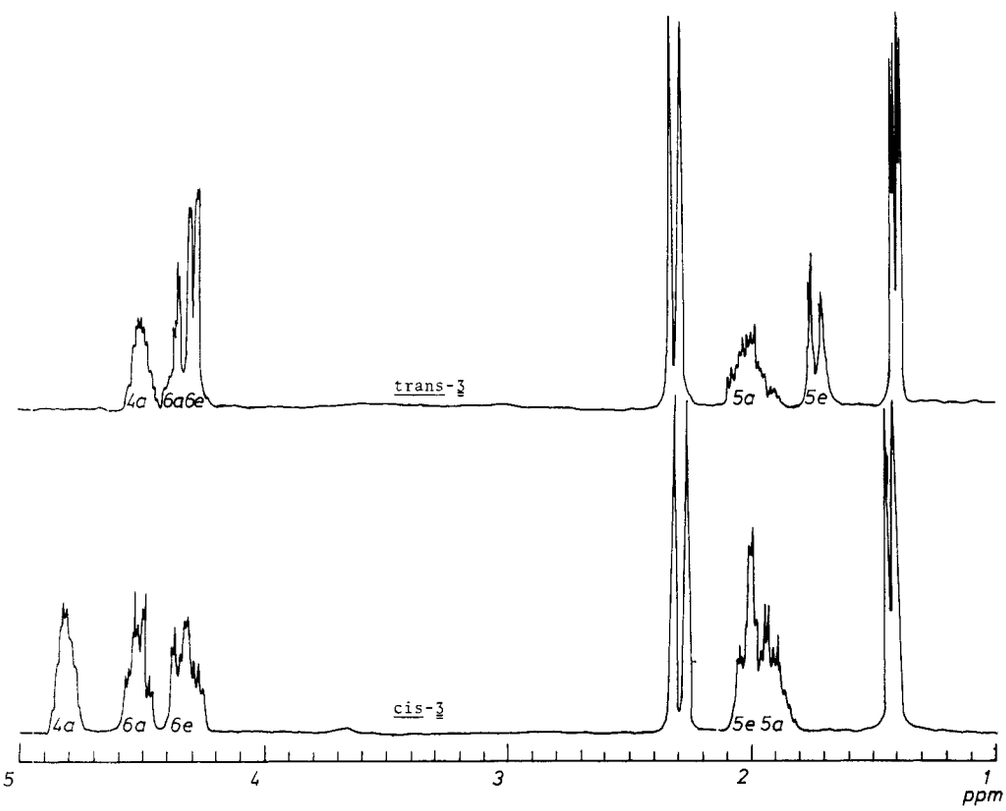
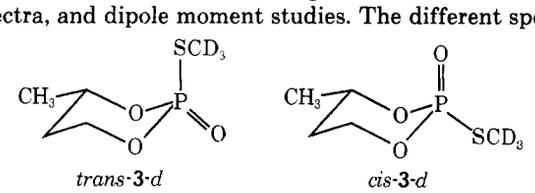


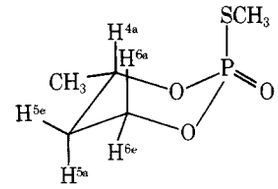
Figure 2. ^1H NMR spectra of the diastereomeric thiol esters (3) in CCl_4 at 300 MHz: top, *trans*-3; bottom, *cis*-3.

The structural assignments described were confirmed by means of ^1H and ^{31}P nuclear magnetic resonance studies, ir spectra, and dipole moment studies. The different spectral properties of the diastereomeric thiol esters 3 were used as a basis for determination of diastereomeric purity.



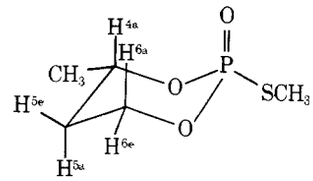
^{31}P NMR spectra of the two isomers show complex multiplets having chemical shifts at −21.0 and −25.8 ppm for *trans*-3 and *cis*-3, respectively. In view of the fact that the spectra are complicated by splitting between phosphorus and the protons of the thiomethyl group the corresponding deuterated diastereomeric esters *trans*- and *cis*-3-*d* were prepared.

Table I. ^{1}H NMR Data for the Solid Isomer of 3 in Carbon Tetrachloride Solution at 300 MHz



Proton	Chemical shift, δ, ppm	Coupling constant (J, Hz) to						
		CH_3	5e	5a	6e	6a	4a	P
CH_3	1.42						6.30	2.20
5e	1.74			14.50	2.25	2.25	2.25	2.25
5a	2.01		14.50		5.80	11.50	11.50	0.50
6e	4.29		2.25	5.80		11.50		20.50
6a	4.35		2.25	11.50	11.50			2.25
4a	4.51	6.30						2.25
CH_3S	2.32							14.25

Table II. ^{1}H NMR Data for the Liquid Isomer of 3 in Carbon Tetrachloride Solution at 300 MHz



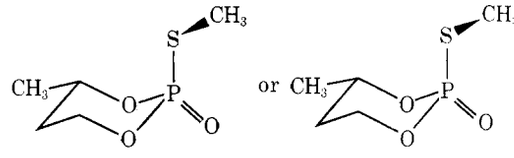
Proton	Chemical shift, δ, ppm	Coupling constant (J, Hz) to						
		CH_3	5a	5e	6e	6a	4a	P
CH_3	1.44						6.20	2.00
5a	1.92			14.70	4.50	10.80	10.50	0.60
5e	2.04		14.70		3.70	3.70	3.60	2.40
6e	4.33		4.50	3.70		11.40		18.00
6a	4.52		10.80	3.70	11.40			8.00
4a	4.82	6.20						4.50
CH_3S	2.32							15.65

The ^{31}P NMR spectrum of the deuterated crystalline isomer (*trans*-**3**-*d*) shows a double multiplet separated by about 20 Hz. According to previous observations[19] such a spectrum is characteristic of a dioxaphosphorinane ring having the chair conformation in which the methyl and phosphoryl groups are situated in equatorial positions. On the other hand the resonance signal for *cis*-**3**-*d* is a broad multiplet which is characteristic of dioxaphosphorinane systems having methyl and phosphoryl groups trans to one another.

More detailed information regarding the conformations of the cyclic thiol esters **3** was obtained by analysis of ^{1}H NMR spectra obtained at 300 Hz in carbon tetrachloride which are essentially first-order spectra (Figure 2). Chemical shifts and coupling constants derived from the spectra are given in Tables I and II.

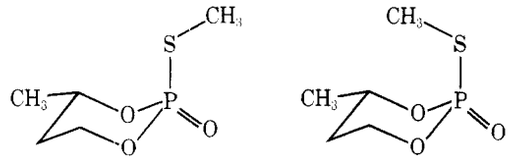
The ^{1}H NMR spectrum of the crystalline isomer consists of six multiplets. The doublet corresponding to three protons at δ 2.32 ppm and the double doublet at δ 1.42 ppm are ascribed to the thiomethyl group and the methyl group bonded to the C_4 carbon atom, respectively. The proton bonded to the C_4 carbon absorbs at lowest field, δ 4.51 ppm, as confirmed by irradiation at the frequency of the ring methyl group. The signals at δ 4.35 and 4.39 ppm correspond to protons bonded to the C_6 carbon atom whereas the single-proton split signal at δ 2.01 ppm having higher coupling constant and the single-proton split signal at δ 1.74 ppm having lower coupling constant corresponded to the axial and equatorial protons bonded to the C_5 carbon atom. The chemical shifts of the ring protons and, most importantly, the very pronounced differences between the long range ^{1}H–^{31}P couplings observed for the axial and equatorial protons of the dioxaphosphorinane[14,20] ring indicate that the ring in *trans*-**3** adopts the chair conformation with the methyl group in equatorial position. The high value of the coupling constant $^4J_{P-CH_3}$ (2.2 Hz) indicates that the methyl group is in the equatorial position whereas the low value of the coupling constant $^3J_{P-4a}$ (2.25 Hz) and the coupling constants J_{4a-5a} and J_{4a-5e} (11.5 and 2.25 Hz) which are typical for vicinal coupling constants J_{anti} and J_{gauche} in the chair conformation indicate that the proton at the C_4 carbon is in the axial position. Similarly the axial and equatorial protons at the C_6 carbon atom are split by phosphorus with low and high coupling constants $^3J_{P-6a}$ = 2.25 and $^3J_{P-6e}$ = 20.5 Hz. The coupling constants for phosphorus and the protons of the C_5 methylene group also show pronounced stereospecificity ($^4J_{P-5a}$ = 0.5 and $^4J_{P-5e}$ = 2.25 Hz).

Since the relative positions of the methyl group and the phosphoryl group in the crystalline isomer follow unambiguously from the method of synthesis it can be assumed that the phosphoryl group occupies the equatorial position whereas the *S*-methyl group is axial. It should be mentioned that low temperature ^{1}H NMR spectra (60 MHz) showed no changes down to −60 °C which is interpreted to mean that *trans*-**3** exists only in one chair conformation. Taking into account the possible existence of rotational isomers due to rotation of the



trans-**3**-*gauche*

μ_{calcd} = 5.59 D



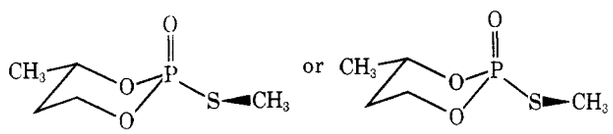
trans-**3**-*syn* μ_{calcd} = 5.01 D

trans-**3**-*anti* μ_{calcd} = 7.05 D

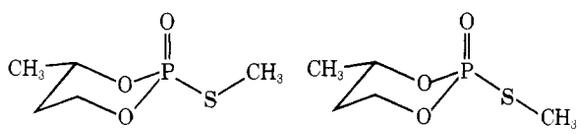
S-methyl group around the P–S bond and our dipole moment studies[21] (μ 5.63 D for *trans*-**3**) we come to the final conclusion that *trans*-**3** exists in a single chair conformation in which the methyl and phosphoryl groups are in equatorial positions whereas the *S*-methyl group is in a position gauche with respect to the phosphoryl group.

Analysis of proton chemical shifts and coupling constants for the liquid isomer *cis*-**3** as shown in Table II leads to the conclusion that the dioxaphosphorinane ring in this isomer also exists in chair conformation with the C_4 methyl group equatorial and the phosphoryl group axial, i.e., that the only difference between *cis*- and *trans*-**3** is the configuration at the phosphorus atom. In agreement with observations reported by Hall and Malcolm[22] the value of the coupling constant for the ring methyl protons with phosphorus obtained in our work ($^4J_{P-CH_3}$ = 2 Hz) is characteristic of an anti relationship between the bond from ring to ring methyl and the endocyclic O–P bond, i.e., it is characteristic of an equatorial ring methyl group in a chair-shaped ring. However, in this case the coupling constant between phosphorus and the proton bonded to the C_4 carbon is 4.50 Hz and that between phosphorus and the protons bonded to the C_6 carbon atom are 18 and 8 Hz. The last value corresponds to coupling with an axial proton but is too high for such coupling. This could be due either to some flattening of dioxaphosphorinane ring in *cis*-**3** or to a slight contribution of the conformer resulting from ring inversion. However, investigation of the temperature dependence of the ^{1}H NMR spectra at 60 MHz in the range from 60 to −60 °C did not reveal any changes in chemical shifts or coupling constants for the C_4 methyl group and the thiomethyl group. Although only a lack of change down to −100 °C would be considered convincing proof for the absence of conformational equilibrium, in our opinion the observed increase of the values of $^3J_{P-4a}$ and $^3J_{P-6a}$ can tentatively be ascribed to ring deformation, particularly in view of the fact that the axial phosphoryl group and the equatorial thiomethyl group are situated in positions opposite to those preferred for these substituents in the 1,3,2-dioxaphosphorinane system.[23,24]

The experimentally determined value of the dipole moment of *cis*-**3** (μ 5.06 D) probably corresponds to a mixture of rotational isomers *cis*-**3**-*gauche* and *cis*-**3**-*anti* in which the latter predominates.



cis-**3**-*gauche* μ_{calcd} = 3.81 D

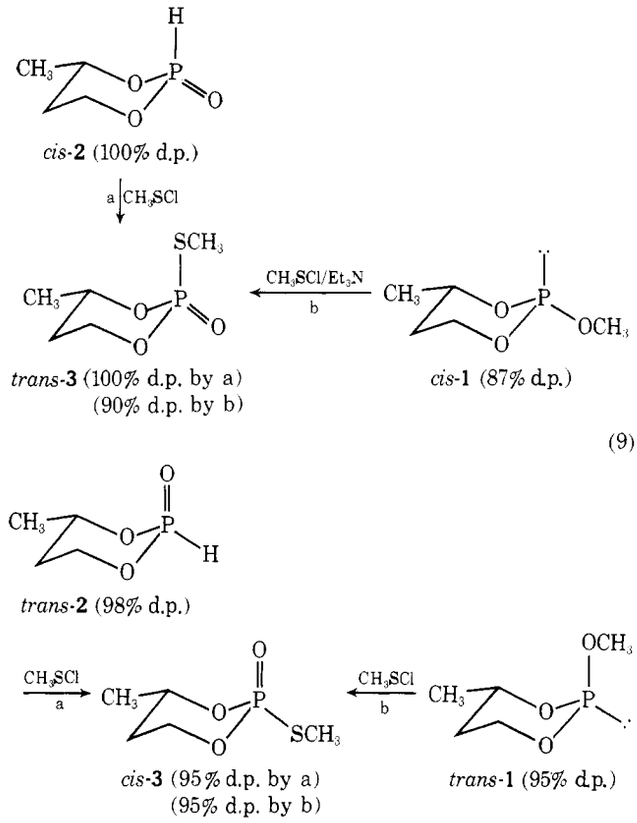


cis-**3**-*syn* μ_{calcd} = 3.10 D

cis-**3**-*anti* μ_{calcd} = 5.42 D

Reaction of Sulfenyl Chlorides with Cyclic Trivalent Phosphorus Compounds. Knowledge of the configuration of the geometric isomers of 2-methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**3**) was used to determine the steric course of the reactions between methylsulfenyl chloride and diastereomeric phosphites **1** and **2**.

It was found that reaction between the more stable isomer *cis*-**2** and methylsulfenyl chloride (route a) at 0 °C in ether or benzene gave *trans*-2-thiomethyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**3**). The same product (*trans*-**3**) was also formed by reaction of the thermodynamically less stable isomer *cis*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (**1**) with methylsulfenyl chloride (route b). In this case the reaction was carried out in the presence of a small amount of triethylamine which was used to scavenge traces of hydrogen chloride present in the sulfenyl chloride. The reaction was



(9)

completely stereospecific. When the reaction was performed in the absence of triethylamine the diastereomeric purity of the resulting *trans*-**3** was lower because of epimerization of the precursor *cis*-**1** caused by traces of hydrogen chloride present in the reaction mixture.[13,14]

Similarly reaction of methylsulfenyl chloride with the thermodynamically less stable phosphite *trans*-**2** and the more stable phosphite *trans*-**1** were completely stereospecific. In both cases the product of reaction was the liquid thiol ester *cis*-**3**.

Since the geometrical structures of the initial phosphites **1** and **2** and the resulting thiol esters **3** are known, the results shown demonstrate that the reactions shown take place with complete retention of configuration at phosphorus.

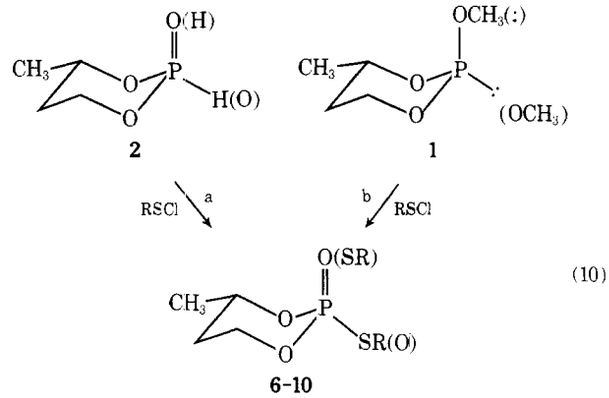
In order to determine whether the particular alkyl or aryl group present in the sulfenyl chloride has an effect on the steric course of the reaction we investigated reactions involving various sulfenyl chlorides. In all cases stereospecific formation of 2-thioalkyl(thioaryl)-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes was observed with retention of configuration at the phosphorus atom (eq 10).

Physical and chemical properties of reaction products are collected in Table III and the corresponding spectral data (^{1}H, ^{31}P NMR, and ir) in Table IV.

Reactions involving 2,4-dinitrophenylsulfenyl chloride require additional comments. We have found that conversion

Table III. Preparation and Physical Properties of *cis*- and *trans*-2-Alkylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes

No.	R	Thiol ester	Bp, °C (mmHg); mp, °C	n^{20}D	Synthetic route	Yield, %	Elemental analyses: Found C	H	P	Calcd C	H	P
3	CH_3	Trans	76–78 (from benzene–cyclohexane)		a	82.3	33.05	6.08	17.42			
					b	66.0	33.10	6.20	17.05			
										32.96	6.09	17.00
										for $C_5H_{11}O_3PS$		
		Cis	90 (0.05)	1.4992	a	67.7	33.33	6.17	17.32			
					b	77.8	33.10	6.00	17.08			
6	CH_3CH_2	Trans	118 (0.1)	1.4937	a	90.3	37.00	6.84	16.23			
										36.73	6.68	15.79
										for $C_6H_{13}O_3PS$		
		Cis	82–84 (0.01)	1.4880	a	51.0	36.88	6.80	15.80			
7	$CH_3CH_2—CH_2$	Trans	107 (0.01)	1.4912	a	62.0	40.13	7.26	14.95			
										39.98	7.19	14.73
										for $C_7H_{15}O_3PS$		
		Cis	91–93 (0.02)	1.4840	a	62.0	39.65	7.20	14.38			
8	CH_3>CH CH_3	Trans	105 (0.02)	1.4886	a	76.2	40.00	7.20	15.13			
										39.98	7.19	14.73
										for $C_7H_{15}O_3PS$		
		Cis	90 (0.02)	1.4880	a	67.0	39.70	7.54	15.21			
9	C_6H_5	Trans	103–104.5 (from benzene–cyclohexane		a	96.0	48.90	5.32	13.00			
					b	77.0	48.64	5.20	13.11			
										49.13	5.36	12.68
										for $C_{10}H_{13}O_3PS$		
		Cis	68–69.5 (from benzene–ether)		a	78.0	49.17	5.36	12.78			
					b	49.0	50.21	5.79	12.83			
10	$2,4\text{-}(NO_2)_2C_5H_4$	Trans	125–127 (from dimethoxyethane–petroleum ether)		a	85.6	35.97	3.48	9.51			
										35.96	3.31	9.27
										for $C_{10}H_{11}O_7N_2PS$		
		Cis			a		36.47	3.40	8.76			



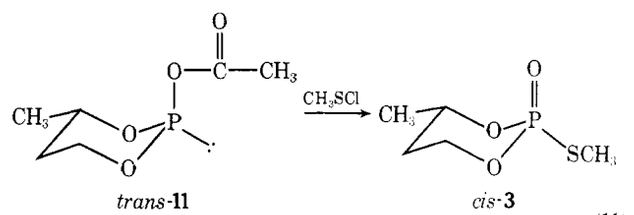
(10)

6, R = Et
7, R = *n*-Pr
8, R = *i*-Pr
9, R = C_6H_5[25]
10, R = $2,4\text{-}(NO_2)_2C_6H_4$

of *cis*- and *trans*-**2** into the corresponding thiol derivatives **10** takes place in high yield with complete retention of configuration. However, in contrast to the thermodynamically more stable *trans*-**10** the corresponding cis isomer could not be isolated in an analytically pure state. This difficulty could be a consequence of the instability of *cis*-**10** and its exceptional sensitivity to moisture which is undoubtedly due to the presence of the 2,4-dinitrophenoxy group which is expected to undergo ready nucleophilic displacement from the phosphorus atom. The same effect is probably responsible for the fact that reaction between *trans*-**1** and 2,4-dinitrophenylsulfenyl chloride is not completely stereospecific and yields 22% of the trans isomer in addition to the expected *cis*-**10**.

The NMR and ir spectral data obtained for diastereomeric thiol esters **3** and **6–10** (Table IV) reveal several interesting relationships between the configuration at phosphorus and certain spectroscopic constants. Thus all of the trans thiol isomers absorb in ^{31}P NMR at a higher field than the corresponding cis isomers. Similarly in ^1H NMR the coupling constants between phosphorus and the protons of the ring methyl groups of the trans isomers are always higher than those of the cis isomers. However, in the case of the cis isomers the coupling is always greater than 1 Hz indicating that the ring methyl group should be equatorial even in these cases. As expected, the infrared absorption of the phosphoryl group (P=O) of the trans isomers appears at a higher wavenumber than that of the corresponding cis isomers thereby confirming the correctness of our configurational assignments.[26]

In extension of this study we examined the reaction between methylsulfenyl chloride and *trans*-2-acetoxy-4-methyl-

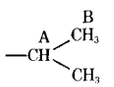
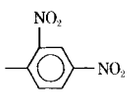


(11)

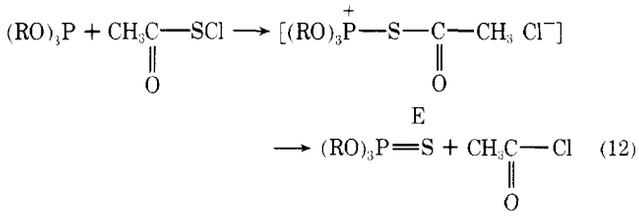
1,3,2-dioxaphosphorinane (**11**) the structure of which has been unambiguously established by Nifantiev.[27] Formation of *cis*-**3** indicates that the configuration at phosphorus in this reaction is also completely retained.

Michalski and Skowrońska[28] have shown that acetylsulfenyl chloride, unlike simple sulfenyl chlorides, reacts with trivalent phosphorus esters to afford the corresponding thionophosphates resulting from the simple addition of sulfur. It is assumed that during the reaction an intermediate phosphonium

Table IV. Spectroscopic Properties of *cis*- and *trans*-2-Alkylthio(arylthio)-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes

Thiol ester			NMR, δ, ppm			IR[c]	
No.	R		^{1}H (J, Hz)[a]	$^4J_{CH_3-P}$	^{31}P[b]	ν(P=O)	ν (other)
3	$-CH_3$	Trans	1.42 (dd, 3 H, $^3J_{CH_3-H}$ = 6.3, $^4J_{CH_3-P}$ = 2.2 Hz); 1.87 (m, 2 H); 2.31 (d, 3 H, $^3J_{CH_3-P}$ = 14.25 Hz); 4.38 (m, 3 H)	2.2	−21.0	1270 vs	1253 vs (P=O) 595 vs (P–S(C))
		Cis	1.44 (dd, 3 H, $^3J_{CH_3-H}$ = 6.2, $^4J_{CH_3-P}$ = 2.0 Hz); 1.98 (m, 2 H); 2.31 (d, 3 H, $^3J_{CH_3-P}$ = 15.65 Hz); 4.56 (m, 3 H)	2.0	−25.8	1260 vs	563 vs (P–S(C))
6	A B $-CH_2-CH_3$	Trans	1.13 (dd, 3 H, $^3J_{CH_3-H}$ = 6.6, $^4J_{CH_3-P}$ = 2.4 Hz); 1.25 (t, 3 H_B, $J_{H_B-H_A}$ = 7.8 Hz); 2.8 (m, 2 H_A)	2.4	−18.5	1280 vs	1265 vs (P=O) 565 vs, 600 vs (P–S(C))
		Cis	1.14 (dd, 3 H, $^3J_{CH_3-CH}$ = 6.75, $^4J_{CH_3-P}$ = 1.8 Hz); 1.22 (t, 3 H_B, $J_{H_B-H_A}$ = 7.8 Hz); 2.8 (m, 2 H_A)	1.8	−22.8	1255 vs	1280 v (P=O) 565 vs, 600 v (P–S(C))
7	A B C $-CH_2-CH_2-CH_3$	Trans	0.97 (dgt, 3 H_C, $J_{H_B-H_C}$ = 7.5 Hz); 1.65 (m, 2 H_B); 1.3 (dd, 3 H, $^3J_{CH_3-H}$ = 6.75, $^4J_{CH_3-P}$ = 2.4 Hz); 2.84 (dt, 2 H_A, $J_{H_A-H_B}$ = 7.2 Hz)	2.4	−18.8	1283 vs	1253 s (P=O) 600 v (P–S–(C))
		Cis	0.94 (dgt, 3 H_C, $J_{H_B-H_C}$ = 7.5 Hz); 1.28 (dd, 3 H, $^3J_{CH_3-H}$ = 6.75, $^4J_{CH_3-P}$ = 1.8 Hz); 1.65 (m, 2 H_B); 2.84 (dt, 2 H_A, $J_{H_A-H_B}$ = 7.2 Hz)	1.8	−22.6	1260 vs	1273 vs (P=O)
8		Trans	1.12 (dd, 3 H, $^3J_{CH_3-H}$ = 6.6, $^4J_{CH_3-P}$ = 2.4 Hz); 1.31 (d, 6 H_B, $J_{H_A-H_B}$ = 7.2 Hz); 3.57 (d sep, 1 H_A, $J_{H_A-H_B}$ = 7.2, $^3J_{P-H}$ = 12 Hz)	2.4	−16.8	1285 vs	1252 s (P=O)
		Cis	1.16 (dd, 3 H, $^3J_{CH_3-H}$ = 6.6, $^4J_{CH_3-P}$ = 1.8 Hz); 1.31 (d, 6 H_B, $J_{H_A-H_B}$ = 7.8 Hz); 3.55 (d sep, 1 H_A, $J_{H_A-H_B}$ = 7.2, $^3J_{P-H}$ = 12.6 Hz)	1.8	−21.0	1260 vs	1278 vs (P=O)
9		Trans	1.01 (dd, 3 H, $^3J_{CH_3-H}$ = 6.6, $^4J_{CH_3-P}$ = 2.5 Hz); 7.4 (m, 5 H, aromatic)	2.5	−11.9	1282 vs	1254 s (P=O) 558 vs, 592 vs (P–S(aromatic))
		Cis	0.89 (dd, 3 H, $^3J_{CH_3-H}$ = 6.75, $^4J_{CH_3-P}$ = 2.1 Hz); 7.4 (m, 5 H, aromatic)	2.1	−15.5	1272 vs	1250 m (P=O) 561 vs, 610 vs (P–S–C(aromatic))
10		Trans	0.80 (dd, 3 H, $^3J_{CH_3-CH}$ = 6.25, $^4J_{CH_3-P}$ = 2.75 Hz)	2.75	−7.0	1290 vs	1248 v (P=O)
		Cis	0.88 (dd, 3 H, $^3J_{CH_3-H}$ = 6.5, $^4J_{CH_3-P}$ = 1.5 Hz)	1.5	−8.2		

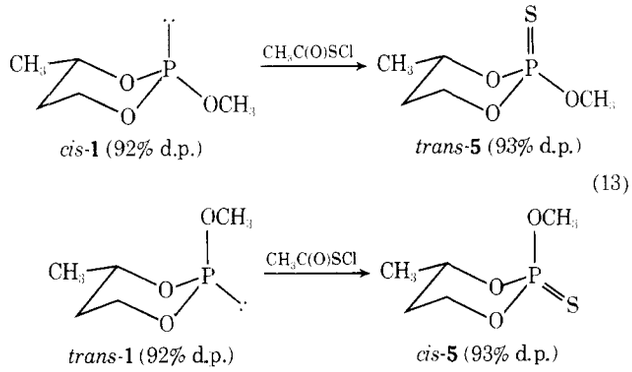
[a] Measured at ambient probe temperatures, JEOL JNM-C60-HL spectrometer. Chemical shifts downfield from Me_4Si as internal standard. Abbreviations used: s, singlet; d, doublet; t, triplet; dt, double triplet, dgt, degenerate triplet; sep, septet; d sep, double septet; m, multiplet. [b] Measured with a JEOL JNM-C-60 HL operating at 24.3 MHz. Chemical shifts downfield from external 85% H_3PO_4. Heteronuclear spin decoupler JNM-SD-HC was used for precise chemical shift determination. [c] Infrared spectra were taken on a UR-10-Zeiss or Spectromom 2000 infrared spectrophotometers. Abbreviations used: vs, very strong; s, strong; m, middle.



(12)

salt E is formed which subsequently suffers attack of chloride ion at the most electrophilic site, namely the carbon atom.

Confirmation of the proposed mechanism and investigation of the steric course of the reaction by means of diastereomeric cyclic phosphites was of interest. For this purpose *cis*- and



(13)

trans-1 were treated with acetylsulfenyl chloride in ether at 0 °C. Diastereomeric purities of both reactants and products as determined by gas chromatography and ^{31}P NMR spectra are shown.

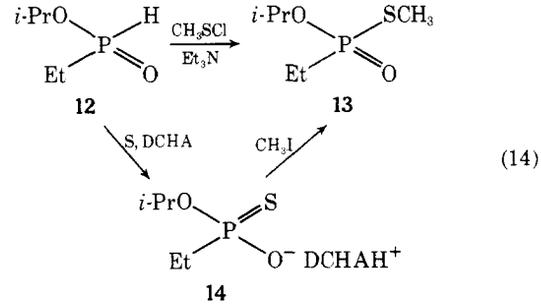
Treatment of *cis*-1 containing 8% of the trans isomer with acetylsulfenyl chloride gave trans thionophosphate **5** containing 7% of the corresponding cis isomer. Analogously *trans*-1 having a diastereomeric purity of 90% gave cis thionophosphate **5** containing 7% of the trans isomer. Thus in this case also addition of sulfur takes place with complete retention of configuration at phosphorus. From a preparative point of view it is noteworthy that this reaction is carried out under very mild conditions.

All of our results corroborate the hypothesis that cyclic phosphites react with a variety of sulfenyl chlorides according to the mechanism involving the intermediate "quasi-phosphonium salt" such as A or E. Further reaction depends on the exact nature of this species. The results of the stereochemical studies do not exclude the possible involvement of the pentacovalent intermediate D which would decompose to the final products with retention of configuration. Intermediates A and D could be in equilibrium with one another. It can be assumed that the reaction of sulfenyl chlorides with phosphites such as **2**, in which the reactive species is phosphite form, >P̈–OH, occurs according to a similar mechanism.

Our stereochemical results exclude a mechanism involving nucleophilic attack of phosphorus on "electropositive" chlorine to give initially the chlorophosphonium salt B. It should be emphasized that even in the reactions involving 2,4-dinitrophenylsulfenyl chloride we observed retention at phosphorus. In the case of this sulfenyl chloride nucleophilic attack on chlorine is expected to be probable in view of stabilization of the negative charge on sulfur by the dinitrophenyl substituent.

Further stereochemical studies are planned on the reactions of phosphites with trichloromethyl- and trifluoromethylsulfenyl chloride since in these cases phosphorus chloroanhydrides and disulfides are formed in addition to thiol esters.

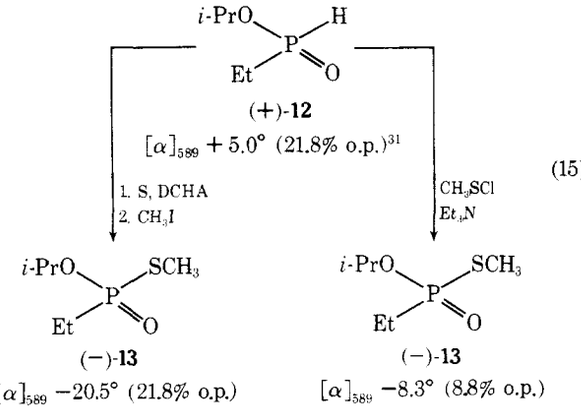
Reaction of Methylsulfenyl Chloride with Optically Active *O*-Isopropyl Ethylphosphinate. It was shown above that reaction of cyclic trivalent phosphorus compounds with a variety of sulfenyl chlorides takes place with retention of configuration at phosphorus. Since steric course and mechanism of reactions of cyclic phosphoroorganic compounds are often different from those of acyclic analogues[29] we have investigated the reaction of methylsulfenyl chloride with optically active *O*-isopropyl ethylphosphinate (**12**) the two optical forms of which were obtained by partial resolution of the racemate via β-cyclodextrin inclusion complexes according to the procedure of Benschop and Van den Berg.[30] All reactions carried out with optically active phosphinates **12** were pre-



(14)

ceded by preliminary experiments with the racemic material. Thus reaction of racemic **12** with methylsulfenyl chloride carried out at 0 °C in the presence of triethylamine gave a good yield of *O*-isopropyl *S*-methyl ethylphosphonothioate (**13**). The same ester **13** was obtained by addition of elemental sulfur to compound **12** in the presence of dicyclohexylamine followed by methylation of the resulting dicyclohexylammonium salt (**14**) by means of methyl iodide.

We have carried out a similar cycle of reactions using the optically active forms of **12**. Phosphinate (+)-**12** having specific rotation $[\alpha]_{589}$ +5.0° and methylsulfenyl chloride gave (−)-**13** having specific rotation $[\alpha]_{589}$ −8.3°. Ester **13** having the same configuration but a much higher specific rotation,



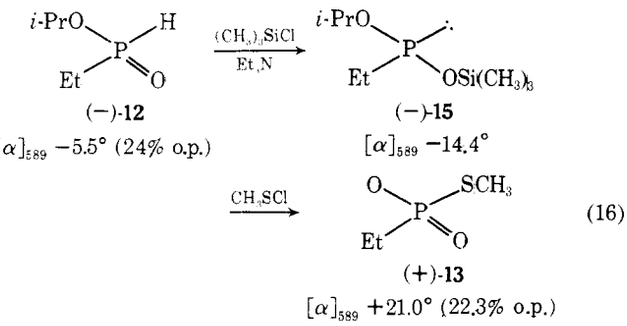
(15)

$[\alpha]_{589}$ −20.5°, is formed as a result of the addition of sulfur to a sample of (+)-**12** having $[\alpha]_{589}$ +5.0° in the presence of dicyclohexylamine followed by methylation of the resulting salt. Since addition of sulfur and methylation of the thio acid anion occur with retention of configuration at phosphorus, the thiol ester (−)-**13** and the initial phosphinate (+)-**12** have the same configuration. Thus reaction of methylsulfenyl chloride with optically active **12** takes place with predominant retention of configuration.

It should be mentioned that the ester **13** formed when the reaction is carried out in the absence of triethylamine is nearly completely racemic. This is probably due to racemization of the starting material **12** caused by hydrogen chloride generated in the reaction, according to the mechanism proposed by Emmick and Letsinger[33] for the racemization of secondary phosphine oxides. Although the use of triethylamine increases the stereospecificity of the reaction of methylsulfenyl chloride with optically active phosphinate **12**, it does not completely inhibit racemization. This is most likely due to the formation and racemization of an intermediate mesomeric phosphonate

anion (>P̈–O⁻ ↔ >P̈=O) which may be formed from **12** by interaction with triethylamine.

Since the optical sensitivity of the >P(O)H system to acids and bases makes it difficult to interpret the steric course of the reaction with methylsulfenyl chloride, we substituted the optically active trimethylsilyl derivative **15** for phosphinate



(−)-**12**
$[\alpha]_{589}$ −5.5° (24% o.p.)

(−)-**15**
$[\alpha]_{589}$ −14.4°

(+)-**13**
$[\alpha]_{589}$ +21.0° (22.3% o.p.)

(16)

12. Benschop[34] has shown that silylation of phosphonates occurs on oxygen and causes no change in configuration at phosphorus.

As expected, reaction of (−)-*O*-isopropyl *O*-trimethylsilyl ethylphosphonite (**15**), $[\alpha]_{589}$ −14.4° [prepared from (−)-**12**, $[\alpha]_{589}$ −5.5°], with methylsulfenyl chloride gave optically active ester (+)-**13** with $[\alpha]_{589}$ +21.0°. Comparison of the specific rotation of the ester prepared by this way with that of the ester obtained by addition of sulfur demonstrates that the reaction takes place with almost complete retention of configuration at phosphorus. Therefore, it is clear that the reactions of simple sulfenyl chlorides with both cyclic and acyclic trivalent phosphorus compounds follow the same steric course, namely complete retention of configuration around the phosphorus atom in the thiol ester product.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded on a Tesla BS-487C 80-MHz spectrometer or JEOL JNM-C-60 HL 60-MHz spectrometer using Me_4Si as an internal standard. The ^{31}P magnetic resonance data were obtained on a JEOL JNM-C-60 HL spectrometer operating at 24.3 MHz. Proton decoupling was accomplished with heteronuclear spin decoupler JNM-SD-HC. Ir spectra were measured on Zeiss-UR-10 or Spectromom 2000 spectrophotometers as KBr disks for solids and pressed films for liquids. GLC analysis was carried out with a Varian Aerograph Model 1520 flame ionization gas chromatograph. Optical activity measurements were made with a Perkin-Elmer 141 photopolarimeter (sensitivity ±0.002°) or with a Hilger and Watts polarimeter (sensitivity ±0.01°). All solvents used were purified according to standard procedures. All reactions involving trivalent phosphorus compounds were carried out under an atmosphere of dry nitrogen.

Synthesis of *trans*-2-Methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3). To a solution of the dicyclohexylammonium salt of *trans*-2-hydroxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (**4**,[14] 3.5 g, 0.01 mol) in 50 ml of benzene an excess of methyl iodide was added. The reaction mixture was allowed to stand at room temperature overnight. The precipitated dicyclohexylammonium iodide was filtered off. The benzene solution was evaporated to afford the crude thiol ester *trans*-**3**. Crystallization from benzene–ether gave 1.4 g (78%) of the pure *trans*-**3**, mp 76–78 °C. Physical and spectroscopic properties are given in Tables I, III, and IV.

Synthesis of *cis*-2-Methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3). To a suspension of the dicyclohexylammonium salt of *cis*-2-hydroxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (**4**,[14] 3.5 g, 0.01 mol) in benzene (50 ml) an excess of methyl iodide was added. The reaction mixture was stirred at room temperature for 24 h and dicyclohexylammonium iodide was then filtered off. Evaporation of filtrate gave the crude *cis*-**3** as an oil which was distilled to afford the pure *cis*-**3**: 1.5 g (82%); bp 90 °C (0.05 mmHg); $n^{20}D$ 1.4992; mp 17 °C. Spectroscopic data of the product are given in Tables II and IV.

cis-**3**-*d* and *trans*-**3**-*d* were prepared in the same manner as described above using trideuteriomethyl iodide.

Isomerization of *trans*-2-Methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (5) to *trans*-3. *trans*-**5** (93% diastereomeric purity) (1.5 g, 0.00825 mol) and methyl iodide were heated in a sealed tube for 3 h at 100 °C. The reaction mixture was then dissolved in benzene and the benzene solution was washed with a 5% aqueous solution of Na_2SO_3 and water. After removal of the solvent crystallization of the residue from benzene–ether yielded 0.5 g (33%) of the diastereomerically pure *trans*-**3**, mp 76–78 °C.

Isomerization of *cis*-2-Methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (5) to *cis*-3. Essentially the same procedure as above yielded from 1.5 g (0.00825 mol) of *cis*-**5** (93% diastereomeric purity) 0.8 g (53.4%) of the 87% diastereomerically pure (^{31}P NMR and GLC assay) *cis*-**3**, bp 90 °C (0.5 mmHg).

General Procedure for Reaction of Alkyl- and Arylsulfenyl Chlorides with Diastereomeric Phosphites 1 and 2. To a stirred solution of 0.03 mol of *cis*- and *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (**1**) or *cis*- and *trans*-2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**2**) in benzene (30 ml), sulfenyl chloride (0.035 mol) in 10 of benzene was added at 0–5 °C. The reaction mixture was stirred at room temperature for 2 h. After removal of solvent the residue was distilled or crystallized to give thioesters which were analyzed by means of ^1H, ^{31}P NMR, and ir spectroscopy and GLC. Yields of the analytically pure products and their physical and spectroscopic properties are collected in Tables III and IV.

In the case of *cis*-**1** as substrate the reaction was carried out in the presence of triethylamine (0.006 mol).

Reaction of *trans*-2-Acetoxy-4-methyl-1,3,2-dioxaphosphorinane (11) with Methylsulfenyl Chloride. Methylsulfenyl chloride (1.65 g, 0.02 mol) in ether (5 ml) was added at 0 °C to a solution of *trans*-**11** (3.56 g, 0.02 mol) in ether (20 ml). The reaction mixture was stirred at room temperature for 1 h. Removal of ether afforded the crude, diastereomerically pure *cis*-2-methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**3**) which was isolated by distillation: 2.8 g (77%); bp 98–102 °C (0.2 mmHg); $n^{20}D$ 1.4992; $\delta_{^{31}P}$ −25.8 ppm.

Reaction of *cis*-2-Methoxy-4-methyl-1,3,2-dioxaphosphorinane (1) with Acetylsulfenyl Chloride. To phosphite *cis*-**1** (92% d.p., 1.5 g, 0.01 mol) in ether (30 ml) acetylsulfenyl chloride (1.1 g, 0.01 mol) in ether (5 ml) was added at −5 °C. After stirring at room temperature for 1 h and removal of ether the reaction product was distilled to give 1.3 g (71.5%) of *trans*-2-methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane (**5**) having 93% of diastereomeric purity (^{31}P NMR and GLC assay): bp 78–80 °C (0.3 mmHg); $n^{20}D$ 1.4892; $\delta_{^{31}P}$ −65.0 ppm (neat).

Reaction of *trans*-2-Methoxy-4-methyl-1,3,2-dioxaphosphorinane (1) with Acetylsulfenyl Chloride. Reaction of *trans*-**1** (90% d.p., 1.5 g, 0.01 mol) with acetylsulfenyl chloride carried out under the same conditions gave after distillation 1.4 g (77%) of *cis*-**5** (93% d.p.): bp 76–78 °C (0.03 mmHg); $n^{20}D$ 1.4930; $\delta_{^{31}P}$ −63.0 ppm (neat).

Reaction of (+)-*O*-Isopropyl Ethylphosphinate (12) with Methylsulfenyl Chloride. To a solution of (+)-**12**, $[\alpha]_{589}$ +5.0° (1.9 g, 0.0145 mol), in 50 ml of benzene, triethylamine (1.47 g, 0.0145 mol) and then methylsulfenyl chloride (1.2 g, 0.0145 mol) were added at 0 °C. The reaction mixture was stirred for 3 h and the precipitated triethylammonium chloride was filtered off. Removal of benzene and distillation of the residue gave 1 g (40%) of (−)-*O*-isopropyl *S*-methyl ethylphosphonothioate (**13**): $[\alpha]_{589}$ −8.3° (*c* 13.49, benzene); bp 69–70 °C (2 mmHg); $n^{20}D$ 1.4595; ^1H NMR (benzene) δ 4.78 (d sep, 1 H, $^3J_{CH-CH_3}$ = 6.4, $^3J_{CH-P}$ = 9.6 Hz), 2.17 (d, 3 H, $^3J_{CH_3-P}$ = 12.6 Hz), 1.72 (m, 2 H), 1.2 (m, 9 H). Anal. Calcd for $C_6H_{15}O_2PS$: C, 39.58; H, 8.29; P, 17.00. Found: C, 39.84; H, 8.43; P, 17.17.

Starting from (−)-**12**, $[\alpha]_{589}$ −4.0°, and methylsulfenyl chloride (+)-**13**, $[\alpha]_{589}$ +12.4° (*c* 9.81, benzene), was obtained.

Synthesis of (−)-*O*-Isopropyl *S*-Methyl Ethylphosphonothioate (13) from (+)-*O*-Isopropyl Ethylphosphinate (12) via Sulfur Addition and Methylation. To a mixture of (+)-**12**, $[\alpha]_{589}$ +5.0° (2 g, 0.0147 mol), and dicyclohexylamine (2.66 g, 0.0147 mol) in ether (50 ml) was added sulfur (0.47 g, 0.0147 mol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. The precipitated dicyclohexylammonium salt of *O*-isopropyl ethylphosphonothioate (**14**) was filtered off and dissolved in benzene (50 ml). The benzene solution was treated with an excess of methyl iodide and the reaction mixture was allowed to stand at 40 °C for 5 h. The precipitated dicyclohexylammonium iodide was filtered off, the benzene solution evaporated, and the residue distilled to give 1.4 g (52.5%) of (−)-**13**: $[\alpha]_{589}$ −20.5°; bp 63 °C (1.7 mmHg); $n^{20}D$ 1.4605. Anal. Calcd for $C_6H_{15}O_2PS$: C, 39.58; H, 8.29; P, 17.00. Found: C, 40.06; H, 8.80; P, 17.38.

Reaction of (+)-**12**, $[\alpha]_{589}$ +5.7°, according to the same procedure gave (−)-**13**, $[\alpha]_{589}$ −23.5°.

Synthesis of (+)-*O*-Isopropyl *S*-Methyl Ethylphosphonothioate (13) from (−)-*O*-Isopropyl Ethylphosphinate (12) via

(−)-*O*-Isopropyl *O*-Trimethylsilyl Ethylphosphonite (15). To a solution of (−)-**12**, $[\alpha]_{589}$ −5.5° (3.4 g, 0.025 mol), in benzene (50 ml), triethylamine (3.78 g, 0.0375 mol) and then trimethylchlorosilane (4.06 g, 0.0375 mol) were added at 0 °C. The reaction mixture was stirred at room temperature for 2 h and the precipitated triethylammonium chloride filtered off. The filtrate was cooled to 0 °C and methylsulfenyl chloride (3.1 g, 0.0375 mol) in benzene (5 ml) was added at this temperature. The reaction mixture was allowed to stand overnight. After the usual workup 2.8 g (61.5%) of (+)-**13**, $[\alpha]_{589}$ +21.0°, was obtained.

Treatment of (−)-**12**, $[\alpha]_{589}$ −5.5° (2.3 g, 0.017 mol), in benzene (30 ml) with triethylamine (2.56 g, 0.025 mol) and trimethylchlorosilane (2.7 g, 0.025 mol) at 0 °C gave after the usual workup (−)-*O*-isopropyl *O*-trimethylsilyl ethylphosphonite (**15**): $[\alpha]_{589}$ −14.4° (neat); bp 40–42 °C (3 mmHg); n^{20}D 1.4156 [very sensitive to moisture, contains small amounts of **12** (up to 5%)]; ^{1}H NMR (benzene) δ 4.1 (d sep, 1 H, $^3J_{CH_3-CH}$ = 6, $^3J_{CH-P}$ = 9.3 Hz), 1.2 (m, 11 H), 0.15 (s, 9 H).

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Registry No.—*cis*-**1**, 7735-85-5; *trans*-**1**, 7735-81-i; *trans*-**3**, 50902-84-6; *cis*-**3**, 50902-83-5; *trans*-**4** DCHA, 35539-47-0; *cis*-**4** DCHA, 26284-89-9; *trans*-**5**, 23168-89-0; *cis*-**5**, 23168-88-9; *trans*-**6**, 60537-84-0; *cis*-**6**, 60537-85-1; *trans*-**7**, 60537-86-2; *cis*-**7**, 60537-87-3; *trans*-**8**, 60537-88-4; *cis*-**8**, 60537-89-5; *trans*-**9**, 53857-47-9; *cis*-**9**, 53909-41-4; *trans*-**10**, 60537-90-8; *cis*-**10**, 60537-91-9; *trans*-**11**, 40781-06-4; (+)-**12**, 31355-97-2; (−)-**12**, 60537-92-0; (−)-**13**, 60537-93-1; (+)-**13**, 60537-94-2; **14**, 60553-53-9; (−)-**15**, 60537-95-3; methyl iodide, 74-88-4; methylsulfenyl chloride, 5813-48-9; acetylsulfenyl chloride, 6405-82-9.

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