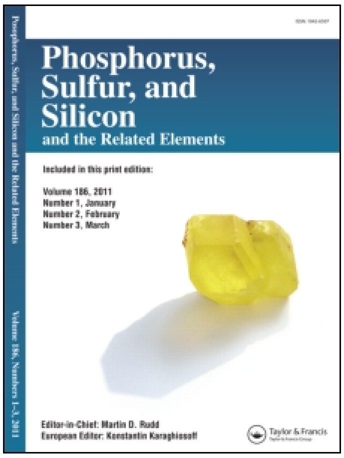


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NEW, UNEXPECTED REACTION OF PHOSPHONOCHLORIDOTHIONATES WITH ALKYL ARYL ETHERS AND ALKYL CHLORIDES UNDER THE FRIEDEL-CRAFTS REACTION CONDITIONS

Jan Omelańczuk[a]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Sienkiewicza 112, Poland

To cite this Article Omelańczuk, Jan(1994) 'A NEW, UNEXPECTED REACTION OF PHOSPHONOCHLORIDOTHIONATES WITH ALKYL ARYL ETHERS AND ALKYL CHLORIDES UNDER THE FRIEDEL-CRAFTS REACTION CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 86: 1, 93 — 102
To link to this Article: DOI: 10.1080/10426509408018393
URL: http://dx.doi.org/10.1080/10426509408018393

Phosphorus, Sulfur, and Silicon, 1994, Vol. 86, pp. 93–102
Reprints available directly from the publisher
Photocopying permitted by license only

A NEW, UNEXPECTED REACTION OF PHOSPHONOCHLORIDOTHIONATES WITH ALKYL ARYL ETHERS AND ALKYL CHLORIDES UNDER THE FRIEDEL-CRAFTS REACTION CONDITIONS

JAN OMELAŃCZUK

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
90-363 Łódź, Sienkiewicza 112, Poland

(Received November 30, 1993; in final form December 20, 1993)

Phosphonochloridothionates have been found to react in the presence of Lewis acids with alkyl aryl ethers to give S-alkyl O-aryl phosphonothiolates and with alkyl halides to form products of the S-alkylation.

Key words: Alkyl aryl ethers; phosphonochloridothionates; alkylation; S-alkyl O-aryl phosphonothiolates; S-alkyl alkyl(aryl) dichlorophosphonium salts; conductivity.

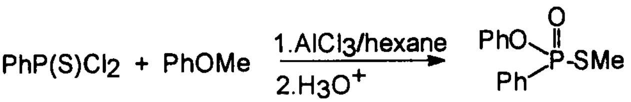
INTRODUCTION

The phosphorylation of aromatic compounds occurring in the presence of Lewis acids constitutes one of the important procedures for the construction of the P-C bond.[1] Although this method has been known for a long time[2] the only exact investigations of the reactions conditions were performed thirty years ago by Maier.[3] The author found that the yields and composition of the products depend mainly on the molar ratio of substrates, temperature and reaction time. The only efficient catalysts of this reaction were found to be those forming stable adducts with thiophosphoryl trichloride, among them $AlCl_3$ or $AlBr_3$. However, in the case of the oxygen or sulfur substituted aromatic hydrocarbons as the substrates (such as anisole, thiophene, furfurol) the reaction with thiophosphoryl chlorides failed.

In this paper we would like to report on a new, unexpected reaction of phosphono- or phosphinochloridothionates with alkyl aryl ethers. Moreover, some new observations concerning alkylation of phosphorylochloridothionates under the influence of the Lewis acids catalysts will be discussed.

RESULTS AND DISCUSSION

In the course of our studies on the synthesis of chiral chlorophosphines it was necessary to prepare chiral, racemic ring substituted phenyl(aryl)phosphinochloridothionates.[4] For this purpose we turned our attention to the method described by Maier.[3] However, we have unexpectedly found that phenylphosphonochloridothionate **1a** reacts with anisole in the presence of aluminium chloride in a quite different way. Thus, refluxing these components in hexane for 3 hr and decomposition of the reaction mixture with ice/HCl gave O-phenyl S-methyl phenylphosphonothiolate as the main product.

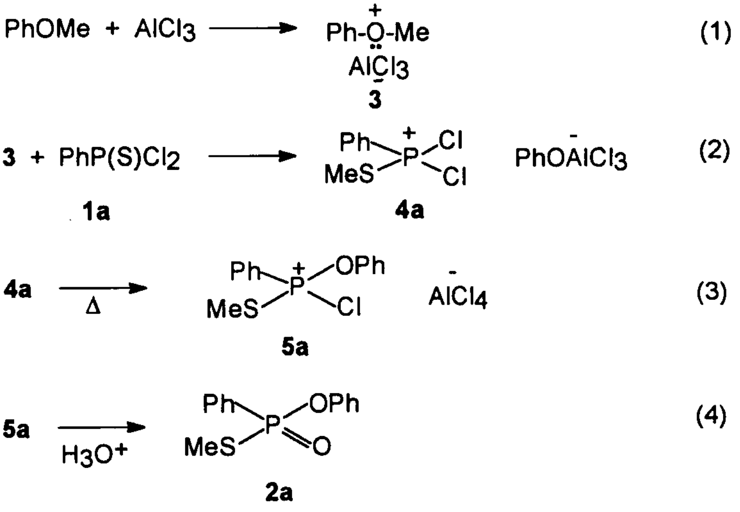


(1)

In order to elucidate this new reaction, its course was monitored by ^{31}P-NMR. In this case 1,2-dichloroethane was used as the solvent since it was expected that it should dissolve better phosphonium salts and aluminum chloride. Thus, after heating under reflux a dichloroethane solution of **1a** with anisole and $AlCl_3$ used in the equimolar ratio for 3 hr three signals were observed in the ^{31}P-NMR spectra. One of them at $\delta = 111.1$ ppm (29%), was ascribed to methylthio phenyldichlorophosphonium salt **4a**, the second at $\delta = 98.3$ ppm (36%) seems to correspond to methylthio-phenoxyphenylchlorophosphonium salt **5a**. The last peak at $\delta = 76$ ppm belongs undoubtedly to the unreacted substrate **1a**. It should be pointed out that the ^{31}P-NMR signals of the salt **4a** and **4b** were known since the corresponding standards were obtained by independent way in the form of trifluoromethanesulfonates.

Furthermore, a 3-hour heating of this mixture causes an increase of the intensity of the peak at $\delta = 98.3$ ppm (53%), corresponding to **5a**, a decrease of the one at $\delta = 111.1$ ppm (17%) corresponding to the salt **4a** and only a slight decrease of the peak of the substrate (30%). This tendency of the intensity changes of these signals was still observed during further reflux of the reaction mixture which after 30 hr contained 65% of salt **5b**, 12% of **1a** and 23% of three other unidentified signals. The signal corresponding to salt **4a** disappeared completely. However, better results of the transformation **1a** → **5a** (83%) were obtained when a half molar excess of anisole and $AlCl_3$ with respect to **1a** were refluxed for 15 hr. Finally the optimal conditions for a full conversion **1a** → **5a** were found when **1a** and a twofold molar excess of anisole and $AlCl_3$ were heated for 17 hr.

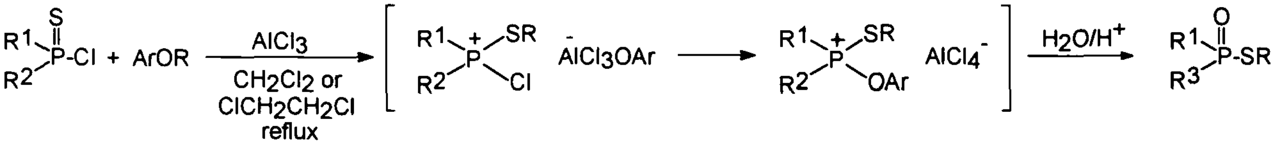
Taking into account the known reactivity of aryl alkyl ethers towards Lewis acids, which form more or less stable oxonium salts[5] and our results presented above, the following course of the reaction between anisole and $AlCl_3$ can be proposed.



Scheme 1

TABLE I

Data of the reaction of phosphono- or phosphinochloridothionates **1** with alkylaryl ethers in the presence of $AlCl_3$



1 **4** **5** **2**

1			Ar	R	1:ArOR :AlCl$_3$	4		5			2		
No	R^1	R^2				No	^{31}P-NMR δ ppm	react. time h	^{31}P-NMR δ ppm CDCl$_3$	% of 5 by ^{31}P-NMR	R^3	^{31}P-NMR δ ppm/ CDCl$_3$	Yield %
a.	Ph	Cl	Ph	Me	1:1:1	a.	111.1	27	98.6	64	PhO	44.8	55
a.	Ph	Cl	Ph	Me	1:1.5:1.5	a.	111.1	15.5	99.3	85	PhO	44.8	74
a.	Ph	Cl	Ph	Me	1:2:2	a.	111.1	17	98.3	100	PhO		
a.	Ph	Cl	Ph	Me	1:2:2	a.	110.6	23	98.0	14^a	PhO		
a.	Ph	Cl	pBr-Ph	Me	1:1:1	b.	111.5	9	99.6	9	pBrPhO		
a.	Ph	Cl	pBr-Ph	Me	1:2:2	b.	110.6	23	99.1	8^b	pBrPhO	45.6	
a.	Ph	Cl	pMePh	Me	1:2:2	c.	110.0	15			pMePhO	44.7	77
a.	Ph	Cl	α-Np	Me	1:1:1	d.	111.1	3	100.3	65	α-NpO	45.4	60
a.	Ph	Cl	Ph	Et	1:2:2	e.	108.3	21	96.5	78	PhO	44.0	74
b.	Et	Cl	Ph	Me	1:2:2	f.	132.7	17	118.2	35^c	PhO	59.6	30
b.	Et	Cl	α-Np	Me	1:2:2	g.		18	119.8	82	α-NpO	60.6	72
b.	Et	Cl	Ph	Et	1:2:2	h.	129.8	50	116.0	47	p-PhO	59.4	40
c.	Ph	Ph	Ph	Me	1:2:2	i.	94.4	5	87.4	90	Ph	44.8	64
c.	Ph	Ph	Ph	Et	1:1:1	j.	92.1	3^d	85.5	62	Ph	43.6	22
d.	PhO	Cl	Ph	Me	1:2:2	k.	69.2	19	40.5	55	PhO	22.2	48

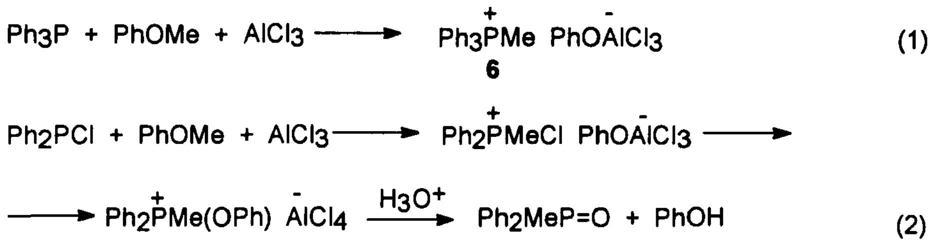
a) 50-55°, 82% of 4; b) 50-55°, 86% of 4; c) 53% of 4; d) 25% of 1.

The first step consists in the formation of the complex **3** which acts in the second step as an alkylating agent towards phosphonochloridothionate **1a** giving the salt **4a**. The third step involves the displacement of a chloride anion by a phenoxy group in the salt **4a** leading to a new salt **5a**, which after hydrolysis affords phenylphosphinothiolate **2a** as the final reaction product. As can be seen from Table I, the reaction is general for phosphono-, phosphino- or aryloxyphosphorochloridothionates and alkyl aryl ethers. However, alkoxyphosphorochloridothionates react with ether under these conditions with decomposition. In the case of an additional oxygen or nitrogen function in the aromatic ring of ethers the reaction does not proceed.

The temperature exerts considerable influence on the **4** → **5** conversion. For instance, heating a mixture of **1a**/anisole/$AlCl_3$ (1:2:2) in 1,2-dichloroethane at 50° for 13 hr gave **4a** in 75% yield and **5a** in only 4% as shown by ^{31}P-NMR.

The same tendency to slow down the conversion **4** → **5** was observed for the electron-withdrawing substituents in the aromatic ring of ethers. Thus, **1a**/p-bromoanisole/$AlCl_3$ (1:2:2) refluxed in ethylene chloride solution for 9 hr yielded **4b** in 23% and **5b** in 9%. This fact may be explained by lower nucleophilicity of the p-bromophenoxy anion towards the phosphorus centre in comparison with the phenoxy one.

The oxonium complex of the type **3** appears to be a weak alkylation agent. For instance, refluxing a mixture of anisole, triphenylphosphine and a twofold molar excess of $AlCl_3$ in ethylene chloride solution for 3.5 hr yields quantitatively triphenylmethylphosphonium salt **6**[6] (^{31}P-NMR δ = 21.4 ppm $CDCl_3$). Similarly, although with some difficulty, Ph_2PCl undergoes alkylation giving after hydrolysis the corresponding phosphine oxide (Equation 2).



$$Ph_3P + PhOMe + AlCl_3 \longrightarrow \underset{\mathbf{6}}{Ph_3\overset{+}{P}Me\ PhO\overset{-}{A}lCl_3} \qquad (1)$$

$$Ph_2PCl + PhOMe + AlCl_3 \longrightarrow Ph_2\overset{+}{P}MeCl\ PhO\overset{-}{A}lCl_3 \longrightarrow$$

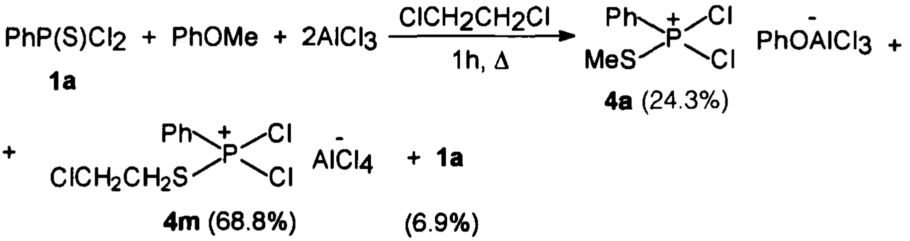
$$\longrightarrow Ph_2\overset{+}{P}Me(OPh)\ \overset{-}{A}lCl_4 \xrightarrow{H_3O^+} Ph_2MeP{=}O + PhOH \qquad (2)$$

Scheme 2

The formation of a complex of the type $PhP^+(S)Cl\ Al^-Cl_4$, which could also explain the reaction under investigation and which was postulated as intermediate for the phosphorylation of aromatic hydrocarbons[7] seems to be less likely as the first step of the title reaction shown in Scheme 1 on the basis of the following observations.

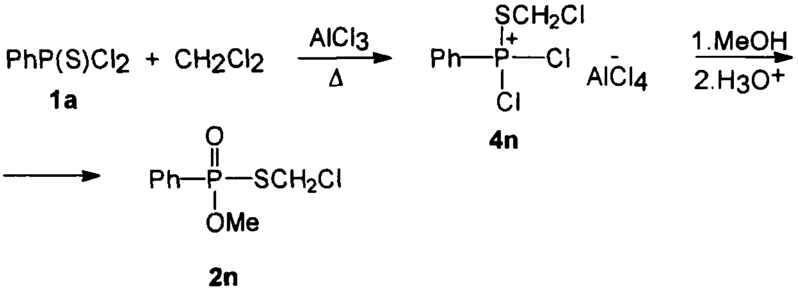
The reaction of **1a** with anisole and phenetole shows two different signals in the ^{31}P-NMR spectra at δ = 111.1 ppm and δ = 108.3 ppm, respectively, which can be ascribed to salts **4**. If the complex $PhP^+(S)Cl\ Al^-Cl_4$,[7] δ = 109.1 ppm were the initial, common intermediate, only one signal should be observed in the ^{31}P-NMR. This is, however, not the case. A more careful investigation of the products revealed the presence of a by-product which was found particularly in the experiments conducted for a long time (ca 30 hr). This by-product appeared to be O-phenyl S-2-chloroethyl phenylphosphonothiolate. It is formed as a result of the alkylation of **1a** by the solvent.

Indeed, when **1a**, anisole and $AlCl_3$ were used in a ratio 1:1:2 and refluxed in ethylene chloride for 1 hr, three peaks at δ = 111.6 (24.3%), 109.6 (68.5%) and 76.8 (6.9%) ppm were detected in the ^{31}P-NMR, corresponding to the salts **4a**, **4m** and **1a**, respectively.

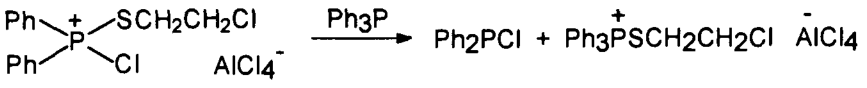

(3)

These results clearly indicate that the alkylation reaction of **1a** by ethylene chloride is faster than that by the complex **3**. It means that the complex **3** is formed rather slowly because of the heterogeneous conditions.

In a separate experiment, a mixture of **1a** and $AlCl_3$ was refluxed in CH_2Cl_2 for 4 hr to give the product which exhibited only one signal in ^{31}P-NMR spectrum (δ = 109.8 ppm) and a characteristic doublet in ^1H-NMR spectra at δ = 5.21 ppm ($^5J_{P-S-C-H}$ = 28.4 Hz). This spectral data are well consistent with the structure of salt **4n** (Equation 4).


(4)

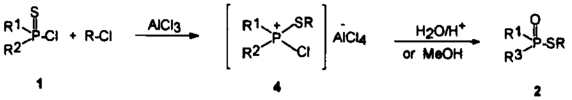
The salts of the type **4** represent very interesting substrates for further transformations. For instance, both chlorine atoms can be replaced by the methoxy group upon treatment with methanol to form a new salt, which after hydrolysis yields phosphonothiolate **2n** (Equation 4). Diphenylchlorophosphine was also obtained in a satisfactory yield when the salt **4** was reacted with triphenylphosphine (Equation 5).[4]


(5)

Some examples of alkylation products and their derivatives are collected in Table II.

TABLE II

Data of the alkylation reaction of **1** with alkyl chlorides in the presence of $AlCl_3$



1			R	4				2		
No	R^1	R^2		No	reaction time h	^{31}P-NMR δ ppm*	% of 4 by ^{31}P-NMR	R^3	^{31}P-NMR δ ppm	yield
a.	Ph	Cl	CH_2CH_2Cl	m.	13	109.4	100	OMe	45.5	60.1
a.	Ph	Cl	CH_2Cl	n.	4.5	109.8	100	OMe	43.3	30
a.	Ph	Cl	CH_2Cl	o.	12	109.5	100	OEt	41.2	29
c.	Ph	Ph	CH_2CH_2Cl	p.	3.5	92.7	100	Ph	44.2	52
c.	Ph	Ph	i-Pr	r.	4	89.8	92	Ph	42.3	67
c.	Ph	Ph	cyclohexyl	s.	13	89.9	61	Ph	43.6	31
d.	PhO	Cl	CH_2CH_2Cl	t.	2.5	89.7	100	OMe	25.5	37
e.	Cl	Cl	CH_2CH_2Cl	u.	12	85.2	100			

In the light of the results presented above and other findings the structure of the complexes described by Maier[7] should be verified. The ^{31}P-NMR chemical shifts of these complexes given by Maier[7] correspond exactly to the shifts of our salts obtained by alkylation of **1** with methylene chloride (see Table III). For example, a freshly prepared 1:1 mixture of **1a** and $AlCl_3$ in CH_2Cl_2 in a NMR tube at room temperature, showed two signals in ^{31}P-NMR at δ = 109.6 ppm (25.5%) and δ = 88.1 ppm (74.5%). The first peak undoubtedly belongs to the salt **4n** and the second one may be ascribed to a complex **1a** · $AlCl_3$. Almost the same value of the chemical shift of a complex **1a** · $AlCl_3$ was noticed when the spectrum was recorded in bromobenzene (δ = 86.9 ppm). Other spectra **1** · $AlCl_3$ measured in bromobenzene (see Table III) are collected in Table III.

TABLE III

Chemical shift of $R^1(R^2)P(S)Cl \cdot nAlCl_3$ ^{31}P-NMR spectra in PhBr and CH_2Cl_2 [7]

1			$AlCl_3$ n	^{31}P-NMR δ ppm in PhBr	^{31}P-NMR δ ppm in CH_2Cl_2	^{31}P-NMR δ ppm 4
Compound	R^1	R^2				
1a	Ph	Cl	1	86.9	109.1	109.8
1a	Ph	Cl	2	94.8		
1c	Ph	Ph	1	83.7	90.4	86.1 (91.3)[a]
1c	Ph	Ph	2	81.5	90.4	
1e	Cl	Cl	1	32.3	84.8	85.2
1e	Cl	Cl	2	31.9		
1e	Cl	Cl	3	30.3		

a. a small amount

In order to confirm the presence of ionic species in a bromobenzene solution of the molar complexes of **1** · $AlCl_3$, the molar conductivity measurements were performed. The value of the molar conductivity of complexes $1 \cdot AlCl_3$ in bromobenzene are by one order lower than that given by Maier.[7]

TABLE IV

Conductances of complex $1 \cdot AlCl_3$ in bromobenzene[a] (conc. 0.59 molare temp. 20°)

Compound	specific conductance χ $cm^{-1}\ \Omega^{-1}$	equivalent conductivity Λ $\Omega^{-1}\ cm^2\ Mol^{-1}$	equivalent conductivity Λ^7 $\Omega^{-1}\ cm^2\ Mol^{-1}$	colour of solution
sat. $PhBr \cdot AlCl_3$	$2.70 \cdot 10^{-7}$		$0.66 \cdot 10^{-7}$	dark pink
$P(S)Cl_3\ AlCl_3$[b]	$12.83 \cdot 10^{-6}$		6.711 $0.396 \cdot 10^{-2}$[c]	dark orange
$PhP(S)Cl_2 \cdot AlCl_3$	$2.71 \cdot 10^{-4}$	0.459	7.674	bright orange
$PhP(S)Cl_2 \cdot 2AlCl_3$[b]	$5.20 \cdot 10^{-4}$		12.38 $0.73 \cdot 10^{-2}$	bright orange
$Ph_2P(S)Cl \cdot AlCl_3$	$2.36 \cdot 10^{-4}$	0.40	3.677	bright yellow
$Ph_2P(S)Cl \cdot 2AlCl_3$[b]	$8.77 \cdot 10^{-4}$		10.37 $0.612 \cdot 10^{-2}$[c]	dark yellow
$(C_6H_5)_3PS\ AlCl_3$	$2.53 \cdot 10^{-4}$	0.429	$0.2723 \cdot 10^{-3}$ $0.92 \cdot 10^{-7}$[c]	bright yellow

a. specific conductance of pure solvent $4.7 \cdot 10^{-7}\ \Omega^{-1}\ cm^{-1}$
b. the complex is not completely dissolved
c. specific conductance

Unfortunately, is not possible to compare the molar conductivity of the complexes $1 \cdot AlCl_3$ with a molar conductivity of any ammonium salts[7] since the latter are extremely insoluble in bromobenzene.

In conclusion, the value of ^{31}P-NMR shifts and conductivity of the complexes $1 \cdot AlCl_3$ given by Maier[7] refer, in fact, to the alkylation products of **1** by methylene chloride and constitute also the examples of a new alkylation reaction of phosphorochloridothionates discussed in the present papers.

EXPERIMENTAL

All boiling and melting points are uncorrected. ^1H-NMR and ^{31}P-NMR spectra were measured with a Bruker AC-200 instrument. MS spectra were obtained with an LKB-900S spectrometer. Conductances were measured by means of a Conductivity Mater type OK-102/1 equipped with a Philips PW electrode with cell constant 0.94. Aryl(diaryl)phosphono- or phosphinochloridothionates were obtained by addition of sulfur to commercially available aryl(diaryl)chlorophosphines.[8] Ethylphosphonochloridothionate was a commercial substrate; $AlCl_3$ was from the Fluka AG company. Solvents were distilled and dried by conventional methods.

S-alkyl O-aryl aryl(alkyl)phosphonothiolates. A general procedure. A mixture of **1**, alkyl aryl ether and $AlCl_3$ in a proportion given in Table I was refluxed in methylene or ethylene chloride for a few hours (Table I). The progress of the reaction was controlled by ^{31}P-NMR. Then, the mixture was poured on crushed ice and acidified with hydrochloric acid (3–5 ml). The organic layer was separated and the water solution was extracted with $CHCl_3$ (2×20 ml). The organic layers were combined and dried over $MgSO_4$. After concentration the residue was purified by distillation or column chromatography. The solvent used and some properties of the corresponding esters are given below.

S-methyl O-phenyl phenylphosphonothiolate **2a**, (hexane), b.p. 140–145/0.2–0.3 mmHg; n_D^{20} 1.5997, ^{31}P-NMR ($CDCl_3$) $\delta = 44.8$ ppm, ^1H-NMR ($CDCl_3$), $\delta = 2.18$ ppm (d, 3, SCH_3, $^3J_{PSCH}$ 13.09 Hz), $\delta = 7.2$–7.6 and 7.9–8.05 ppm (2m, 10, Har).

Anal. for $C_{13}H_{13}O_2PS$ Calcd. C, 59.08; H, 4.96; P, 11.72
Found C, 58.90; H, 4.94; P, 11.68
MS m/e 264 (M^+), 217 ($Ph(PhO)PO^+$), 171 ($PhP(O)SMe^+$), 124 ($PhP(O)^+$, 77 (Ph^+).

S-methyl O-p-bromophenyl phenylphosphonothiolate, **2b** (ethylene chloride) isolated by TLC (toluene: acetone:i-PrOH 4:1:0.2) in 92% purity, ^{31}P-NMR (CDCl$_3$) $\delta = 45.6$ ppm, (an impurity at $\delta = 12.92$ ppm). ^{1}H (CDCl$_3$), $\delta = 2.18$ ppm (d, 3, SCH$_3$, $^3J_{PSCH}$ 12.21 Hz), $\delta = 7.15$–7.60 and 7.90–8.05 ppm (2m, 10, Har), MS (gas chromatography) m/e (rel intensity) 343 (M$^+$, 3.5) 342 (14.8), 341 (8), 174 (9), 169 (11), 142 (4), 142 (7), 141 (100), 77 (48).

S-methyl O-p-tolyl phenylphosphonothiolate, **2c** (ethylene chloride), b.p. 122/0.3 mmHg, n_D^{20} 1.5940, ^{31}P-NMR (CDCl$_3$) $\delta = 44.7$ ppm, ^{1}H (CDCl$_3$) $\delta = 2.14$ ppm (d, 3, SCH$_3$, $^3J_{PSCH}$ 10.22 Hz), $\delta = 2.29$ ppm (s, 3, CH$_3$), $\delta = 7.05$–7.25, 7.40–7.60 and 7.90–8.02 ppm (3m, 9, Har).

Anal. for $C_{14}H_{16}O_2PS$ Calcd. C, 60.24; H, 5.77; P, 11.09
Found C, 59.99; H, 5.46; P, 11.46

S-methyl O-α-naphthyl phenylphosphonothiolate **2d** (ethylene chloride) b.p. 220 (temp of oven)/0.2 mmHg, n_D^{20} 1.6492, ^{31}P-NMR (CDCl$_3$), $\delta = 45.4$ ppm; ^{1}H (CDCl$_3$), $\delta = 2.19$ ppm, (d, 3, SCH$_3$, $^3J_{PSCH}$ 14.20 Hz), $\delta = 7.50$–8.18 ppm (m, 12, Har).

Anal. for $C_{17}H_{15}O_2PS$ Calcd. C, 64.95; H, 4.81; P, 9.85
Found C, 65.03; H, 4.83; P, 10.27

S-ethyl O-phenyl phenylphosphonothiolate **2e** (without solvents, 100°) b.p. 140°/0.3 mmHg, n_D^{20} 1.5913, ^{13}P-NMR (CDCl$_3$), $\delta = 44.0$ ppm; ^{1}H (CDCl$_3$), $\delta = 1.20$ ppm (t, 3, CH$_3$, $^3J_{HCCH}$ 7.41 Hz, $^4J_{PSCCH}$ 0.47 Hz), $\delta = 2.71$–2.90 ppm (m, 2, CH$_2$), $\delta = 7.13$–8.04 ppm (m, 10, Har).

Anal. for $C_{14}H_{15}O_2PS$ Calcd. C, 60.41; H, 5.43; P, 11.13
Found C, 60.72; H, 5.39; P, 11.76

S-methyl O-phenyl ethylphosphonothiolate **2f** (hexane) b.p. 125/0.2 mmHg, n_D^{20} 1.5503; ^{31}P-NMR (CDCl$_3$), $\delta = 59.6$ ppm, ^{1}H (CDCl$_3$), $\delta = 2.24$ ppm (d, 3, SCH$_3$, $^3J_{PSCH}$ 12.71 Hz), $\delta = 1.32$ (2t, 3, CH$_3$, $^3J_{PCCH}$ 22.52 Hz, $^3J_{HCCH}$ 7.63 Hz), $\delta = 2.15$ ppm (m, 2, CH$_2$), $\delta = 7.14$–7.35 ppm (m, 5, Har).

Anal. for $C_9H_{13}O_2PS$ Calcd. C, 49.99; H, 6.06; P, 14.32
Found C, 50.42; H, 6.11; P, 13.99

S-methyl O-α-naphthyl ethylphosphonothiolate **2g** (ethylene chloride) purified by column chromatography (hexane and hexane-toluene as eluents) and distillation b.p. 160–175 (temp. of oven)/0.2 mmHg, n_D^{20} 1.6123 ^{31}P-NMR (CDCl$_3$), $\delta = 60.6$ ppm, ^{1}H (CDCl$_3$), $\delta = 2.25$ ppm, (d, 3, SCH$_3$, $^3J_{PSCH}$ 12.77 Hz), $\delta = 1.45$ ppm, (2t, 3, CH$_3$, $^3J_{PCCH}$ 22.52 Hz, $^3J_{HCCH}$ 7.65 Hz), $\delta = 2.32$ ppm, (m, 2, CH$_2$), 7.26–8.09 ppm (m, 7, Har).

Anal. for $C_{13}H_{15}O_2PS$ Calcd. C, 58.63; H, 5.68; P, 11.63
Found C, 58.49; H, 5.62; P, 12.20

S-ethyl O-phenyl ethylphosphonothiolate **2h** (ethylene chloride), b.p. 150° (temp. of oven)/15 mmHg, n_D^{20} 1.5390, ^{31}P-NMR (CDCl$_3$), $\delta = 59.4$ ppm, ^{1}H (CDCl$_3$), $\delta = 1.21$ ppm (t, 3, $\underline{CH_3}CH_2S$, $^3J_{HCCH}$ 7.46 Hz), $\delta = 1.31$ ppm (2t, CH$_3$, $^3J_{PCCH}$ 22.54 Hz, $^3J_{HCCH}$ 7.48 Hz), $\delta = 2.04$–2.19 ppm (m, 2, CH$_2$), $\delta = 2.76$–2.88 ppm (m, 2, S-CH$_2$), $\delta = 7.13$–7.32 ppm (m, 5, Har), MC m/e (rel intensity) 230 (19.2 M$^+$), 170 (8.2), 141 (16.7), 109 (22.5), 105 (23.3), 94 (100).

S-methyl diphenylphosphinothiolate **2i** (ethylene chloride) b.p. 160° (temp. of oven)/0.1 mmHg, n_D^{20} 1.6335, ^{31}P-NMR (CDCl$_3$), $\delta = 45.5$ ppm, ^{1}H-NMR (CDCl$_3$), $\delta = 2.22$ ppm (d, 3, SCH$_3$, $^3J_{PSCH}$ 12.08 Hz, $\delta = 7.42$–7.54 and 7.82–7.93 (2m, 10, Har).

Anal. for $C_{13}H_{13}OPS$ Calcd. C, 2.89; H, 5.28
Found C, 62.33; H, 5.06

S-ethyl diphenylphosphinothiolate **2j** (without solvents, 100°) purified by TLC (toluene:Aceton, 4:1), m.p. 70–74°, lit[9] 75–6°, ^{31}P-NMR (CDCl$_3$), $\delta = 43.6$ ppm, ^{1}H (CDCl$_3$), $\delta = 1.28$ ppm, (t, 3, CH$_3$, $^3J_{HCCH}$ 7.48); $\delta = 2.81$ (2q, 2, $^2J_{PCH}$ 10.71 Hz); $\delta = 7.42$–7.53 ppm and 7.81–7.93 ppm (2m, 10, Har).

S-methyl O,O-diphenyl phosphorothiolate **2k** (ethylene chloride) b.p. 180° (temp. of oven)/0.1 mmHg, n_D^{20} 1.5759; lit.[10], b.p. 145–7/0.01 mmHg, n_D^{20} 1.5765, ^{31}P-NMR (CDCl$_3$), $\delta = 22.2$ ppm, ^{1}H (CDCl$_3$), $\delta = 2.29$ (d, 3, SCH$_3$, $^3J_{PSCH}$ 16.14 Hz), $\delta = 7.04$–7.29 ppm (m, 10, Har).

Alkylation of phosphino- or phosphonochloridothionates with alkyl halides/AlCl$_3$. A general procedure. A mixture of **1** and AlCl$_3$ in a molar ratio 1:1 to 1:2 was refluxed in methylene chloride, ethylene chloride or hexane with the corresponding alkyl chloride (some excess) for a few hours (Table II). After ^{31}P-NMR control, an alcohol (5 ml) was added at low temp. ($-30 \div -50$). The mixture was then warmed to room temp. and stirred for 2 days. The isolation of the products was achieved by decomposition of the mixture with ice/HCl, extraction with CHCl$_3$ (2 × 30 ml) and drying over MgSO$_4$. After concentration the residue was distilled or chromatographed. Some properties of thiolates **2** are presented below.

O-methyl S-2-chloroethyl phenylphosphonothiolate **2m**. 1a: $AlCl_3$ (1:2), $ClCH_2CH_2Cl$ (15 ml); b.p. 140 (temp. of oven)/0.2 mmHg; n_D^{20} 1.5681; ^{31}P-NMR ($CDCl_3$), δ = 45.5 ppm, ^{1}H ($CDCl_3$), δ = 3–3.15 ppm (m, 2, $-SCH_2-$), δ = 3.61 ppm (t, 2, CH_2Cl, $^3J_{HCCH}$ 7.40 Hz), δ = 3.87 (d, 3, OMe, $^3J_{POCH}$ 12.48 Hz), δ = 7.46–7.58 and 7.79–7.91 ppm (2m, 5, Har).

Anal. for $C_9H_{12}O_2PSCl$ Calcd. C, 43.12; H, 4.82; P, 12.36
Found C, 43.13; H, 4.90; P, 12.48

O-methyl S-chloromethyl phenylphosphonothiolate **2n**. 1a: $AlCl_3$ (1:1.5), CH_2Cl_2 (20 ml); b.p. 140° (temp. of oven)/0.2 mmHg, n_D^{20} 1.5788, ^{31}P-NMR ($CDCl_3$), δ = 43.3 ppm, ^{1}H ($CDCl_3$), δ = 3.89 ppm, (d, 3, OMe, $^3J_{POCH}$ 12.67 Hz), δ = 4.79 ppm, (d, 2, CH_2, $^3J_{PSCH}$ 16.36 Hz), δ = 7.43–7.59 and 7.77–7.90 ppm (2m, 5, Har), MC m/e (rel intensity) 236 (7, M^+), 191 (60), 193 (15), 155 (100), 77 (14).

O-ethyl S-chloromethyl phenylphosphonothiolate **2o**. 1a: $AlCl_3$ (1:2), CH_2Cl_2 (20 ml); b.p. 120° (temp. of oven)/0.3 mmHg, n_D^{20} 1.5622; ^{31}P-NMR ($CDCl_3$), δ = 41.2 ppm, ^{1}H ($CDCl_3$), δ = 1.42 ppm (t, 3, $-CH_3$, $^3J_{HCCH}$ 7.09 Hz), δ = 4.24–4.39 (m, 2, OCH_2), δ = 4.83 ppm (d, 3, SCH_2Cl, $^3J_{PSCH}$ 17.64 Hz), δ = 7.43–7.58 and 7.81–7.93 (2m, 5, Har).

Anal. for $C_9H_{12}O_2PSCl$ Calcd. C, 43.12; H, 4.83; P, 12.36
Found C, 43.76; H, 5.06; P, 12.37

S-2-chloroethyl diphenylphosphinothiolate **2p**. 1b: $AlCl_3$ (1:1.5), $ClCH_2CH_2Cl$ (15 ml); b.p. 175° (temp. of oven)/0.2 mmHg, ^{31}P-NMR ($CDCl_3$), δ = 44.2 ppm, ^{1}H ($CDCl_3$), δ = 3.04–3.15 ppm (2t, 2, SCH_2, $^3J_{HCCH}$ 7.76 Hz, $^3J_{PSCH}$ 12.67 Hz, δ = 3.63 ppm (t, 2, CH_2Cl, $^3J_{HCCH}$ 7.76 Hz), δ = 7.43–7.57 and 7.81–7.92 ppm (2m, 10, Har), MS m/e (rel intensity), 297 (1.4 M^+), 234 (1.4 M^+), 234 (100), 201 (97), 110 (3.3), 77 (5.4).

S-i-Propyl diphenylphosphinothiolate **2r**. 1b: $AlCl_3$ (1:1), hexane (20 ml) and iPrCl (5 ml); b.p. 170 (temp of oven)/0.05 mmHg, m.p. 107–110°; ^{31}P-NMR ($CDCl_3$), δ = 42.3 ppm, ^{1}H-NMR ($CDCl_3$), δ = 1.34 ppm (d, 6, $C(CH_3)(CH_3)$, $^3J_{HCCH}$ 6.82 Hz), δ = 3.36–3.47 ppm (m, 1, CH=), δ = 7.41–7.52 and 7.82–7.93 (2m, 10, Har).

Anal. for $C_{15}H_{17}OPS$ Calcd. C, 65.19; H, 6.20; P, 11.21
Found C, 64.78; H, 6.21; P, 11.20

S-cyclohexyl diphenylphosphinothiolate **2s**. 1b: $AlCl_3$ (1:1), $C_6H_{11}Cl$ (15 ml) temp. 40–50°; b.p. 180 (temp of oven)/0.05 mmHg, m.p. 81–85°, ^{31}P-NMR ($CDCl_3$), δ = 43.6 ppm, ^{1}H-NMR, δ = 1.22–1.67 and 1.90–1.98 ppm (2m, 10, Hcyelohexyl), δ = 3.21–3.36 ppm (m, 1, $-S-CH$), δ = 7.43–7.53 and 7.81–7.93 ppm (2m, 10, Har).

Anal. for $C_{18}H_{21}OPS$ Calcd. C, 68.33; H, 6.69; P, 9.79
Found C, 68.50; H, 6.79; P, 9.63

S-2-chloroethyl O-methyl O-phenyl phosphorothiolate **2t**. 1d: $AlCl_3$ (1:2), $ClCH_2CH_2Cl$ (15 ml); b.p. 125–140 (temp of oven)/0.05–0.01 mmHg, n_D^{20} 1.5400, ^{31}P-NMR ($CDCl_3$), δ = 25.5 ppm, ^{1}H ($CDCl_3$), δ = 3.17 ppm (2t, CH_2S, $^3J_{PSCH}$ 18.12 Hz, $^3J_{HCCH}$ 7.49 Hz, δ = 3.59 ppm (t, 2, CH_2Cl, $^3J_{HCCH}$ 7.49 Hz), δ = 3.88 (d, 3, OMe, $^3J_{POCH}$ 12.92 Hz), δ = 7.20–7.36 ppm (m, 5, Har).

Anal. for $C_9H_{12}O_3PSCl$ Calcd. C, 40.53; H, 4.53; P, 11.61
Found C, 40.68; H, 4.60; P, 12.29

Methyltriphenylphosphonium salt **6**. A mixture of Ph_3P (9.0 g, 0.0345 m), $AlCl_3$ (46 g, 0.0345 m) and anisole (3.7 g, 0.0345 m) was refluxed in 30 ml $ClCH_2Cl$ for 12 hr. ^{31}P-NMR chemical shift of the salt **6** was observed at δ = 22.12 ppm, lit^{10} for Ph_3PMeX^-, δ from 18.8 to 22.7 ppm. The solution was directly used for ^{31}P-NMR study of the displacement of a chlorine atom by the phenoxy group in phosphono- and phosphinochloridothionates.^{6}

Diphenylmethylphosphine oxide from diphenylmethylchlorophosphonium salt. A mixture of Ph_2PCl (0.82 g, 3.75 mM), $AlCl_3$ (0.5 g, 3.75 mM) and anisole (5 ml) was refluxed for 2 hr. Then, the mixture was poured on ice/HCl and extracted with chloroform (3 × 15 ml). The soln was dried over Me_3SO_4 and after concentration, the residue was distilled and redistilled to give 0.4 g (50% yield) diphenylmethylphosphine oxide, m.p. 114–117, lit.^{11}, m.p. 111.5–112; ^{31}P-NMR ($CDCl_3$), δ = 30.6 ppm.

Diphenylchlorophosphine from diphenylphosphinochloridothionate **1c**. Diphenylphosphinochloridothionate **1c** (4.9 g, 0.0195 m) and $AlCl_3$ (2.6 g, 0.0195 m) were refluxed in dichloroethane (20 ml) for 1 hr. Then, Ph_3P (5.1 g, 0.0195 m) was added and the mixture was refluxed for 1.5 hr. Dichloroethane was evaporated in vacuum and from the residue a crude product was distilled off (4.2 g); redistillation of this product gives diphenylchlorophosphine 2.7 g (63% yield) b.p. 103–5/0.2 mmHg, n_D^{20} 1.6360, ^{31}P-NMR ($CDCl_3$), δ = 81.4 ppm, lit.^{12}, b.p. 114/0.6 mmHg, n_D^{20} 1.6365, ^{31}P-NMR, δ = 81.6 ppm.

S-2-chloroethyltrichlorophosphonium salt **4u**. Thiophosphoryl chloride **1e** (2.3 g, 0.0136 m) and $AlCl_3$ (4 g, 0.030 m) were refluxed in ethylene dichloride (15 ml) for 12 hr. The solution exhibited one peak in ^{31}P-NMR spectrum at $\delta = 85.2$ ppm. The salt was neither isolated nor transformed.

ACKNOWLEDGEMENT

Ms. A. Sobczak is thanked for technical assistance with the experimental work.

REFERENCES AND NOTES

1. M. Field, R. Schmutzler and S. C. Peake in "Organic Phosphorus Compounds," ed. G. M. Kosolapoff and L. Maier, Wiley Interscience a Division John Wiley and Sons Inc., New York, London, Sydney, Toronto, Vol. 4, p. 155.
2. A. Michaelis, *Justus Liebiegs, Ann. Chem.*, **315,** 43 (1901).
3. L. Maier, *Helv. Cim. Acta*, **47,** 120 (1964); L. Maier pat. germ. 1 238 024 (1967)/C.A. 90934 t (1967).
4. J. Omelańczuk, *Heteroatom Chem.*, **3,** 403 (1992).
5. G. Dittus, H. Kröper and H. Meerwein, Sauerstoff Verbindungen Teil 3 in Methoden der Organischen Chemie ed. Georg Thieme Verlag, Stuttgart, 1965, pp. 145, 157.
6. The salt **6** exchanges easily the chlorine atom by the phenoxy group in phosphonochloridothionates as evidenced by ^{31}P-NMR.
7. L. Maier, *Chimica*, **18,** 401 (1964); L. Maier, *Zeitschrift f. anorg. allg. Chemie*, **345,** 29 (1966).
8. Reference 1, p. 166.
9. R. S. Edmundson, Dictionary of Organophosphorus Compounds, ed. Chapman and Hall, 1988, London, New York, p. D-01082.
10. G. Hilgetag, G. Lehman, A. Martin, G. Schramm and H. Teichmann, *J. Prakt. Chemie*, **8,** 207 (1959).
11. L. Horner, H. Hoffmann, H. G. Wippel, G. Hassel, B. Nippe and H. Oediger, *Chem. Ber.*, **91,** 45 (1958).