SYNTHESIS OF ISOTHIOCYANATOPHOSPHORANES AND ISOTHIOCYANATOPHOSPHONIUM SALTS VIA OXIDATIVE ADDITION OF THIOCYANOGEN AND LIGAND SUBSTITUTION. NOVEL REAGENTS FOR CONVERTING HYDROXY GROUPS INTO THIOCYANATE AND ISOTHIOCYANATE FUNCTIONS UNDER MILD CONDITIONS

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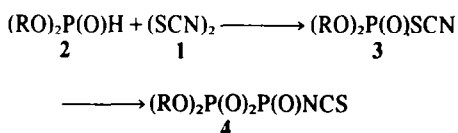
Abstract—The oxidative addition of thiocyanogen to triphenylphosphine has been investigated by ^{31}P NMR spectroscopy showing the formation of the isothiocyanatophosphonium salt **8**. The analogous reaction between thiocyanogen and alkyl o-phenylene phosphites **7** leads to diisothiocyanatophosphoranes **9**. The same products were prepared via ligand substitution from the corresponding chlorophosphonium salt **12** and alkyldichloro-o-phenylene phosphoranes **13** by the action of potassium thiocyanate in the presence of 18-crown-6-ether or more conveniently using lead thiocyanate. The phosphonium salt **8** and phosphoranes **9** were employed as convenient novel reagents for converting hydroxy groups into thiocyanate and isothiocyanate functions with high stereoselectivity under very mild conditions. The efficient synthesis of acylisothiocyanates RCONCS, R₂P(O)NCS and R₂P(S)NCS via addition of thiocyanogen to mixed anhydrides is of special interest.

The chemistry of halogen addition to tricoordinate phosphorus compounds has been the subject of intensive investigations over the years since the studies in this area were initiated in the nineteenth century. More recently, exploratory and mechanistic investigations of those reactions have become the targets of detailed ^{31}P NMR studies.[1] In contrast, reactions of pseudohalogens with the tricoordinate phosphorus systems were, until our present work, a void field.[2] Our expectation was that the reactions of P(III) compounds with pseudohalogens, and especially with those containing disulphide redox systems might held mechanistic, stereochemical and synthetic interest. For this reason we initiated exploratory studies starting with the classic pseudohalogen, thiocyanogen (SCN)₂ **1**. The oxidative additions of **1** to P(III) compounds gave highly reactive isothiocyanatophosphonium salts **8** and diisothiocyanatophosphoranes **9**. At the same time these products were found in our studies of ligand displacements in the halogenophosphonium salts **12** and the halogenophosphoranes **13**.[2] These two areas of work became complementary in both structural studies and synthetic uses of the products.

RESULTS AND DISCUSSION

Addition of thiocyanogen to triphenylphosphine and o-phenylene alkylphosphites

The reactions of **1** with dialkyl phosphites **2** and the related systems >P(O)H, which lead to the isothiocyanidates **4**, have been investigated by Michalski and Wieczorkowski[3] and reinvestigated recently in this laboratory.[4]

$$(RO)_2P(O)H + (SCN)_2 \longrightarrow (RO)_2P(O)SCN$$
$$\quad\quad\; 2 \quad\quad\quad\quad 1 \quad\quad\quad\quad\quad\quad 3$$

$$\longrightarrow (RO)_2P(O)_2P(O)NCS$$
$$\quad\quad\quad\quad\quad 4$$

It has been demonstrated that this reaction proceeds via
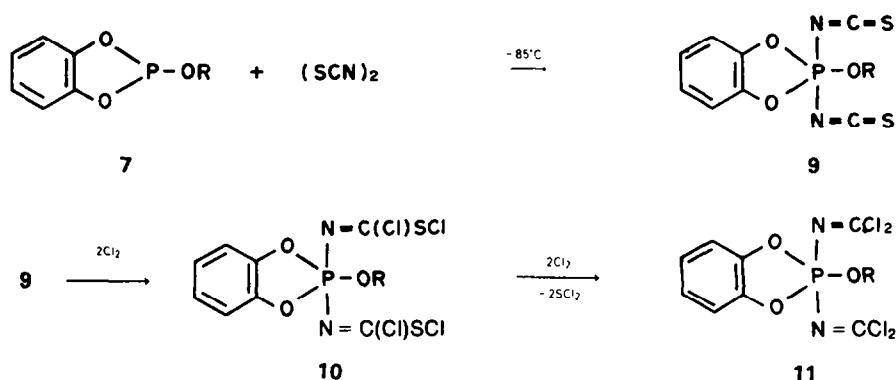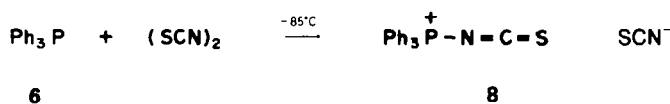
phosphorothiocyanidates **3** which rearrange into **4** under the reaction conditions.

The reaction of trialkyl phosphites (RO)₃P with **1** studied by the same authors has been demonstrated to be more complex.[5] The major isolated products were **4**, trialkylphosphorothionates (RO)₃P=S and alkyl thiocyanate RSCN **5**. Spectroscopic techniques of that time did not allow the study of this system in more detail. Using the recently developed techniques of low temperature FT ^{31}P NMR spectroscopy to follow reactive intermediates we repeated the earlier work and found it essentially correct. However, our main efforts were directed towards the other models such as tert-phosphines and o-phenylene alkyl phosphites **7**.

Thiocyanogen (SCN)₂ **1** reacts with triphenylphosphine Ph₃P **6** and phosphites **7** below the ambient temperature. For example **6** and **7** react readily with **1** even at −85°C. In the liquid nitrogen, however, no detectable reaction takes place, making it possible to bring the substrates together without reaction. In a typical experiment the tricoordinate compounds **6** and **7** were dissolved in methylene chloride or ethyl chloride, the solution was could in the liquid nitrogen and a small excess of the thiocyanogen solution in methylene chloride was added. When the temperature was allowed to rise to −85°C, the ^{31}P NMR spectra indicated the formation of isothiocyanatophosphonium salt **8** in the case of **6** and diisothiocyanatophosphorane **9** in the case of **7**.

The structure of **8** and **9** was also evident from their IR spectra. Compounds **8** and **9** were stable at −40°C and in the case of **9** (R=Ph) even at the room temperature. Phosphoranes **9** underwent a smooth reaction with the elemental chlorine at −80°C in toluene in a manner typical for compounds containing the isothiocyano group.

The reaction was carried out by treating **9** with an appropriate amount of chlorine to give the adduct **10** which was allowed to react without isolation with ano-

$$Ph_3P \; + \; (SCN)_2 \; \xrightarrow{-85°C} \; Ph_3\overset{+}{P}-N=C=S \qquad SCN^-$$

6   **8**

$$7 \; + \; (SCN)_2 \; \xrightarrow{-85°C} \; 9$$

7   **9**

$$9 \; \xrightarrow{2Cl_2} \; 10 \; \xrightarrow[-2SCl_2]{2Cl_2} \; 11$$

9   **10**   **11**

ther two moles of chlorine to give the phosphorane **11**. The five-coordinate structures of **9**, **10** and **11** were clearly evident from their ^{31}P NMR spectra (see Table 1).

Synthesis of triphenylisothiocyanatophosphonium salt 8 and o-phenylenealkyl diisothiocyanatophosphoranes 9 via ligand substitution
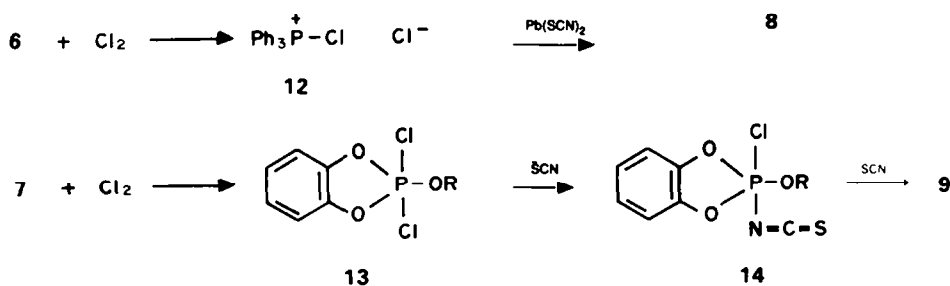
The commercially available triphenyl chlorophosphonium chloride **12**, which may also be prepared *in situ* from the elemental chlorine and triphenyl phosphine,

was converted into the phosphonium salt **8** as follows: the salt **12** prepared at $-40°C$ from **6** and the elemental chlorine in the methylene chloride solution was allowed to react with a small excess of potassium thiocyanate in the presence of 18-crown-6-ether at $-30°C$ and gave **8** in a quantitative yield. In a similar manner the dichlorophosphorane **13**, prepared *in situ* from the phosphite **7**, gave **9** by a stepwise ligand substitution. The intermediate chloroisothiocyanatophosphorane **14** was clearly detected using ^{31}P NMR spectroscopy.

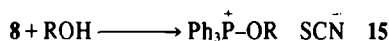Interestingly enough it proves much easier to convert

Table 1. ^{31}P NMR data of phosphoranes and phosphonium salts

Compounds		^{31}P NMR δ, ppm; J, in Hz
9a	$C_6H_4O_2P(NCS)_2OEt$	-77
9b	$C_6H_4O_2P(NCS)_2OCH_2Bu^t$	-76
9c	$C_6H_4O_2P(NCS)_2OCH(Me)C_6H_{13}$	-77
9d	$C_6H_4O_2P(NCS)_2Bu^t$	-41
9e	$C_6H_4O_2P(NCS)_2NEt_2$	-79
10a	$C_6H_4O_2P|N=C(Cl)SCl|_2OEt$	-39
10b	$C_6H_4O_2P|N=C(Cl)SCl|_2OCH_2Bu^t$	-40
11a	$C_6H_4O_2P(N=CCl_2)_2OEt$	-42
11b	$C_6H_4O_2P(N=CCl_2)_2OCH_2Bu^t$	-43
12a	$C_6H_4O_2PCl(NCS)OEt$	-54
15a	$Ph_3\overset{+}{P}OEt \; \overset{-}{S}CN$	$+61.7$
15b	$Ph_3\overset{+}{P}OBu \; \overset{-}{S}CN$	$+61.5$
18	$Ph_3\overset{+}{P}NCS \; \overset{-}{S}CN$	$+39$
23a	$C_6H_4O_2\overset{+}{P}(NCS)OC(O)Me \; \overset{-}{S}CN$	$+29$
24	$C_6H_4O_2\overset{+}{P}(NCS)O-P(O)(OEt)_2$ $\overset{-}{S}CN$	-9.9 (d); $+3.3$ (d) $^2J_{POP}$ 20 Hz
25a	$C_6H_4O_2\overset{+}{P}(NCS)OP(S)(OEt)_2 \; \overset{-}{S}CN$	$+54.3$ (d); -1.85 (d) $^2J_{POP}$ 25.5
25b	$C_6H_4O_2\overset{+}{P}(NCS)OP(S)(Ph)Bu^t \; \overset{-}{S}CN$	$+111.9$ (d); $+1.4$ (d) $^2J_{POP}$ 42.17

compounds 12 and 13 into the corresponding isothiocyanato derivatives 8 and 9 by treatment with a 20% excess of lead thiocyanate in the in the absence of the crown ether under the same reaction conditions. The spectral properties of 8 and 9 prepared by oxidative addition of the thiocyanogen and by ligand substitution were identical.
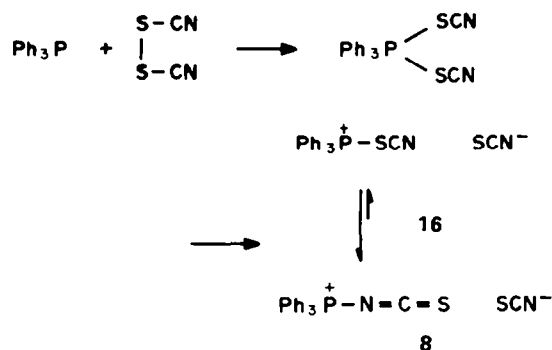
The isothiocyanatophosphonium salt 8 can be readily converted into the alkoxyphosphonium salt 15 by reaction with an appropriate alcohol ROH at −30°C. The synthetic applicability

$$8 + ROH \longrightarrow Ph_3\overset{+}{P}\text{-OR} \quad \overset{-}{SCN} \quad 15$$

of this unstable salt will be discussed in a later section devoted to the applications of 8 and 9 in converting the –OH groups into the –SCN or –NCS functions. The data presented here clearly indicate the pentacoordinate nature of the structures 9, 10, 11 and 14; they do not give, however, an unambigous answer concerning the positions of ligands in the trigonal bipyramide involved. In view of a lack of spectral differences between the isothiocyanato ligands in 9 one could either assume that both are situated in an equatorial position or a fast ligand exchange takes place below the NMR time scale. IR and ^{13}C NMR spectroscopy also failed to distinguish between the isothiocyanato ligands. It is interesting to note that introduction of a group with a known tendency to occupy the equatorial position,[6] such as t-butyl or dialkylamino, did not induce any essential changes in ^{31}P NMR spectra. Therefore another possibility should also be considered: in spite of different spacial arrangements, the isothiocyano ligands may have ^{31}P NMR shifts and IR ν_{NCS} frequencies which are indistinguishable under the experimental conditions used.

The first step in the oxidative addition of thiocyanogen 1 to tricoordinate phosphorus compounds merits particular attention. Although the concerted addition[7] with
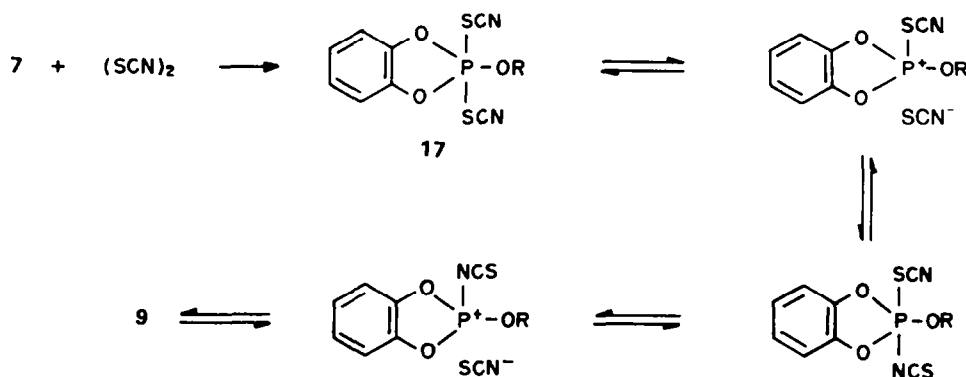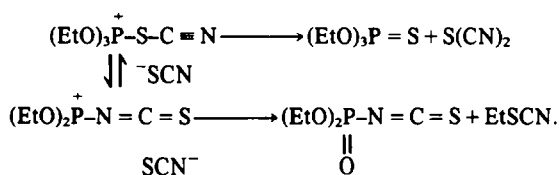
the formation

of a phosphorus-sulphur bond is depicted in the above scheme, the alternative process involving direct formation of the phosphonium salt 16 cannot be ruled out. It seems most likely that the isomerisation of the structure 16 into 8 proceeds via nucleophilic displacement at the phosphourus centre by the ambident SCN⁻ nucleophile. A scheme describing the conversion of the intermediate 7 into 9 would be of the same nature.

The return of ion pairs to the pentacoordinate structures proceeds according to the SHAB principle with the formation of the stronger phosphorus-nitrogen bond. The isomerisations postulated here are reminiscent of thiocyanidato-isothiocyanidato isomerisation > P(O)SCN ⟶ > P(O)NCS discovered in this laboratory.[8]

Although the isothiocyanato phosphonium salts and phosphoranes are only spectroscopically detectable species in these systems, it is necessary to assume the existance of a fast equilibrium between structures 16 and 8 strongly shifted towards the latter. Such equilibria would explain in a satisfactory manner the reaction between triethyl phosphite (EtO)$_3$P and 1 leading to the parallel formation of the phosphorothionate (EtO)$_3$P = S

and the phosphoroisothiocyanidate $(EtO)_2P(O)N=C=S$.

$$(EtO)_3\overset{+}{P}-S-C \equiv N \longrightarrow (EtO)_3P = S + S(CN)_2$$

$$\Updownarrow \ ^-SCN$$

$$(EtO)_2\overset{+}{P}-N=C=S \longrightarrow (EtO)_2P-N=C=S + EtSCN.$$
$$SCN^- \qquad\qquad\qquad\qquad \underset{O}{\overset{\|}{}}$$
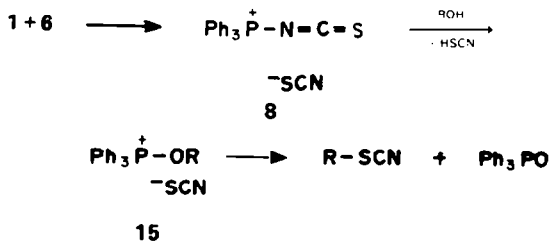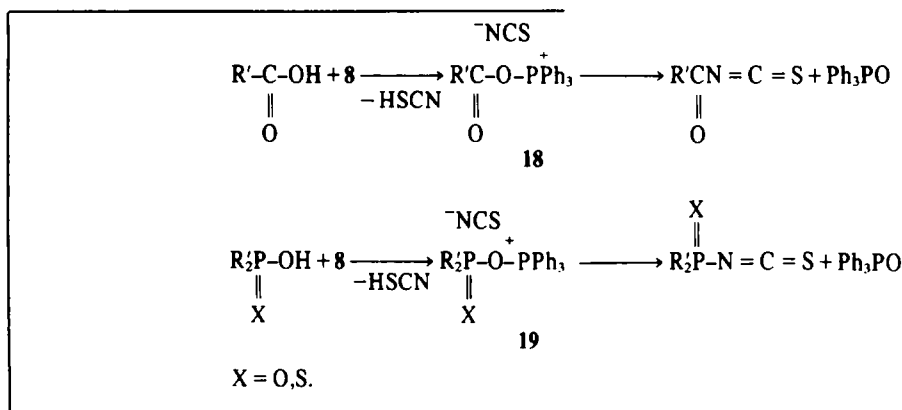
It would also explain the observation by Tamura that the adduct $Ph_3P(SCN)_2$ acts as a cyanating reagent towards indoles and pyroles with formation of triphenylphosphine sulphide $Ph_3P = S$.[9]

$$Ph_3\overset{+}{P}-S-C \equiv N \ SCN^-$$
$$+$$

$$\longrightarrow \quad Ph_3P = S$$

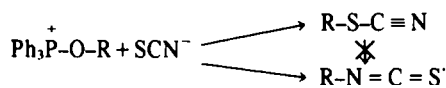$$+ \quad HSCN$$

$$+ \quad N \equiv C$$

This cyanation reaction seems to be catalysed by the thiocyanic acid formed.

Application of thiocyanogen adducts with triphenylphosphine 8 and o-phenylenealkylphosphites 9 for converting hydroxy groups into thiocyanate and isothiocyanate functions

The isothiocyanatophosphonium salt **8** prepared *in situ* from triphenylphosphine and thiocyanogen reacts smoothly with alcohols to produce the corresponding thiocyanates. The sequence of reactions can be outlined as follows:

The experimental procedure involved the preparation of thiocyanogen in methylene chloride by addition of a calculated amount of bromine to a suspension of dry lead thiocyanate. Led bromide and polymeric substances were decanted and the solution of **8** was allowed to react with the appropriate primary alcohol at $-30°C$. The reaction mixture was allowed to warm to the room temperature and the thiocyanates formed were separated either by distillation or with the aid of silica gel chromatography. Secondary alcohols give a mixture of thiocyanates and isothiocyanates. In contrast, tertiary alcohols react with **8** to give the isothiocyanates. Control experiments indicated that, in the case of secondary alcohols, isothiocyanate formation is related to the ambident character of the SCN^- anion and the "hardness" of the R-group as alkylating electrophile, rather than to an isomerisation $R-SCN \longrightarrow R-NCS$ as suggested by Tamura.[9]

$$Ph_3\overset{+}{P}-O-R + SCN^- \begin{array}{c} \longrightarrow R-S-C \equiv N \\ \cancel{} \\ \longrightarrow R-N=C=S \end{array}$$

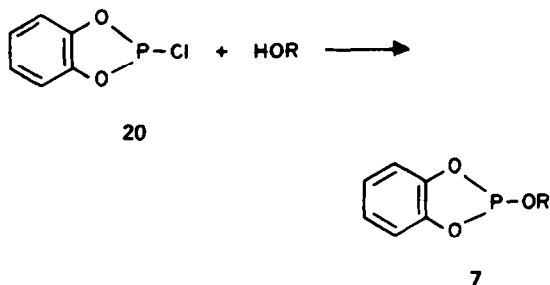The formation of alkyl isothiocyanates was observed in the case of substituted benzyl derivatives which ought to display a pronounced S_N1 character. The formation of alkyl isothiocyanates is accompanied by the inversion of configuration at the chiral carbon centre. This is in full agreement with the mechanistic scheme presented above.
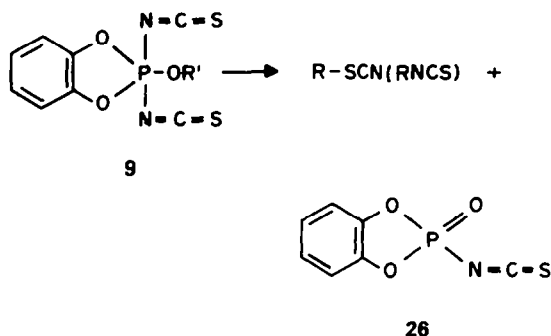
The reaction of **8** with carboxylic acids and phosphorus oxo and thioacids provides a new access to acyl isothiocyanates $R'-CO-N=C=S$, $R_2'P(O)N=C=S$, $R_2'P(S)N=C=S$. The yields of acyl isothiocyanates are, however, lower than those of alkyl thiocyanates and usually do net exceed 50%. The mechanistic interpretation of the reaction with acids is analogous to that presented for alcohols. The intermediate anhydride structures **18** and **19** decompose by the nucleophilic attack of the thiocyanate anion on the carbonyl or phosphinyl group.

$$R'-\underset{O}{\overset{\|}{C}}-OH + 8 \xrightarrow[-HSCN]{} R'C-\underset{O}{\overset{+}{O}}-\overset{^-NCS}{PPh_3} \longrightarrow R'CN=C=S + Ph_3PO$$
$$\underset{18}{}$$

$$R_2'\underset{X}{\overset{\|}{P}}-OH + 8 \xrightarrow[-HSCN]{} R_2'P-\underset{X}{\overset{+}{O}}-\overset{^-NCS}{PPh_3} \longrightarrow R_2'\overset{\overset{X}{\|}}{P}-N=C=S + Ph_3PO$$
$$\underset{19}{}$$

$$X = O,S.$$

$$1 + 6 \longrightarrow Ph_3\overset{+}{P}-N=C=S \xrightarrow[\cdot HSCN]{ROH}$$
$$^-SCN$$
$$\mathbf{8}$$

$$Ph_3\overset{+}{P}-OR \longrightarrow R-SCN + Ph_3PO$$
$$^-SCN$$
$$\mathbf{15}$$

The nucleophilic displacements by SCN^- anion which apparently take place in these reactions are most likely to proceed according to the SHAB rules. This means that the carbon–nitrogen bond or phosphorus-nitrogen bond are formed directly without formation of the intermediate R-COSCN or $R_2'P(X)SCN$ structures. Attempts to characterize the phosphonium intermediates **18** and **19** by low temperature ^{31}P NMR spectroscopy were not successful.
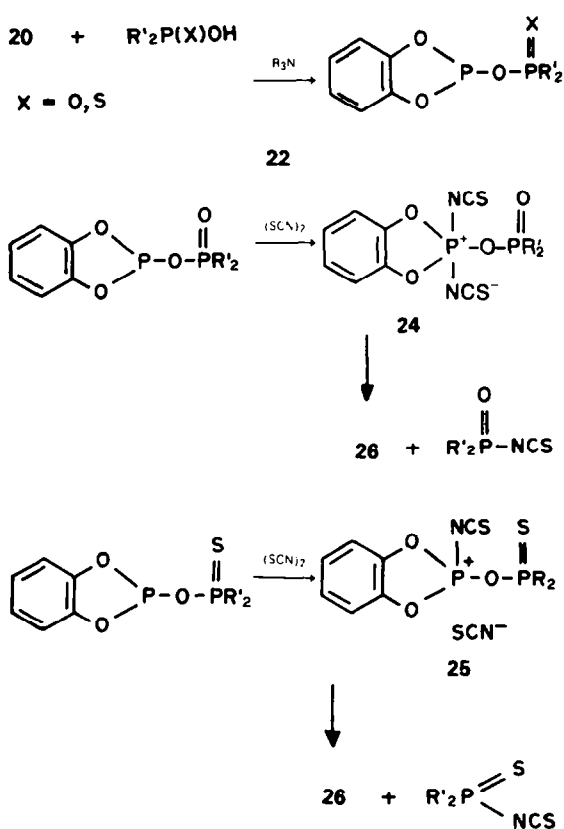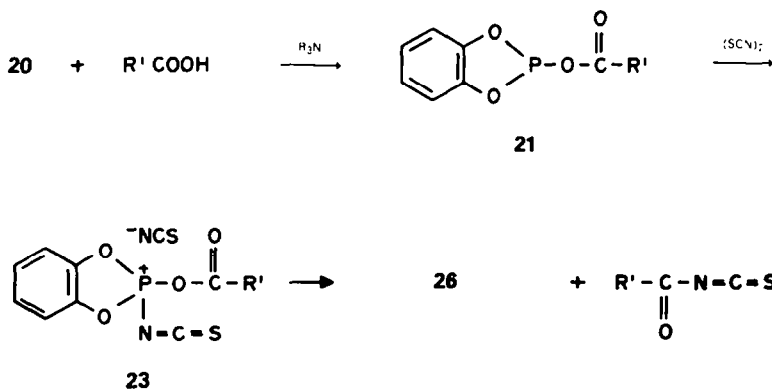
The thermal decomposition of the diisothiocyanato-phosphoranes **9**, prepared either by the addition of thiocyanogen or ligand substitution, offer an alternative and attractive route to thiocyanates and isothiocyanates. The necessary starting phosphites **7** can be readily obtained in a quantitative yield under very mild conditions from the chloridite **20** and the appropriate alcohol in the presence of a tertiary amine. This reaction may be followed by ^{31}P NMR spectroscopy and there is no need for isolation of **7**.

After preparation of **9** in the manner described in the first part of this paper, the reaction mixture is warmed to $-30°C$, kept at this temperature for 0.5 h and then brought to the ambient temperature.

Alkyl thiocyanates or isothiocyanates are isolated either by distillation or silica-gel chromatography in high yields. Formation of thiocyanates and isothiocyanates is accompanied by the inversion of configuration at the chiral carbon atom. The mixed anhydrides **21** and **22** are also readily available by condensation of the chloridite **20** with the corresponding acid at 0°C in the presence of a tertiary amine. Isolation of **21** and **22** is not recommended because of their instability.

After the addition of thiocyanogen in the methylene chloride solution below 0°C the reaction mixture is allowed to warm to the room temperature. The acyl isothiocyanates are obtained here by this method in very good yield. It is of interest to note that according to the ^{31}P NMR spectra the compounds **23** and **24** and **25** have phosphonium structure.

The termal decomposition of **9** and **24** involves most likely a phosphonium intermediates **25** which undergo the S_N2 or S_N1 type displacement reactions leading to thiocyanates or isothiocyanates.

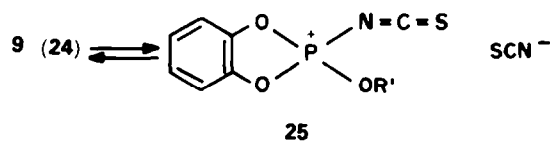Table 2. Preparation of thiocyanato and isothiocyanato derivatives

Alcohols and Acids	Methods	Yield[a]/%	RSCN[b]/%	RNCS[b]/%	b.p., °C/mmHg RSCN	RNCS
MeOH	A	75	100		50–1/12	
	B	80	100		45–6/10	
EtOH	A	80	100		50/11	
	A'	85	100		48/20	
	B	85	100		49/20	
	B'	83	100		52/23	
Pr^{n}OH	A	84	99		72/10	
Bu^{t}CH$_2$OH	A	85	60	40	98–9/16	95–6/17
	A'	82	60	40	102/17	92–3/15
	B	80	100		102–3/17	
	B'	85	100		95–6/15	
PhCH$_2$OH	A	90	100		138–9/2	
	B	95	100		142/3	
	B'	92	100		135–6/1	
Pr^{i}OH	A	80	76	5	140–1	137–8
MeCH(OH)(CH$_2$)$_5$Me [α]$_D^{20}$ +9.5°	A	85	78 [α]$_D^{20}$ −45°	22 [α]$_D^{20}$ −56.2°	98,5–9/4	95–6/4
	A'	85	75 [α]$_D^{20}$ −32.3°	25 [α]$_D^{20}$ −56.9°	95–6/3	91–9/3
	B	86	91 [α]$_D^{20}$ −35.09°	9 [α]$_D^{20}$ −56.5°	97–8/4	95–6/4
MeC(O)OH	A'	72		100		40/21
	B	50		100		38/20
	B'	51		100		45/23
CH$_3$O-p-C$_6$H$_4$C(O)OH	A'	75		100		85–89/0.01
(EtO)$_2$P(O)OH	A'	65		100		63–5/0.03
	B	55		100		69–70/0.05
	B'	54		100		68–9/0.05
(EtO)$_2$P(S)OH	A'	75		100		60–1/0.02
	B	55		100		58–9/0.01
(Bu^{t}CH$_2$O)$_2$P(S)OH	A'	80		100		90–3/0.1
Bu^t(Ph)P(S)OH	A'	92		100		85–6/0.05

[a] Total yields of pure compounds are based on the alcohols and acids used
[b] The percentage of RSCN and RNCS refer to their ratio in the products

All products have ir, nmr spectra consistent with the assigned structures; the microanalyses were in satisfactory agreement with the calculated values.

EXPERIMENTAL

Solvents were purified by conventional methods. Octan-2-ol was resolved as described.[10] Alkyl 1,2-phenylene phosphites was synthesised by a known method.[11] Mixed anhydrides were prepared as described by Michalski et al.,[12] ^{31}P NMR data: $C_6H_4O_2POC(O)Me$, δ + 129.2 ppm; $C_6H_4O_2POC(O)C_6H_4$-p-OCH_3, δ + 130.6 ppm; $C_6H_4O_2POP(O)OEt)_2$, δ + 123.8 ppm, − 10.9 ppm; $C_6H_4O_2POP(S)(OEt)_2$, δ + 123.8 (d) ppm, + 54.2 (d) ppm, $^2J_{POP}$ 25.3 Hz; $C_6H_4O_2POP(S)(Ph)Bu^t$, δ + 128.6 ppm, + 97.3 ppm. All reactions were done in sealed tubes and standard vacuum techniques were used throughout. ^{31}P NMR Spectra were recorded at 24.3 MHz with a JEOL R-60H Spectrometer operating in the pulsed Fourier transform mode. A heteronuclear spin decoupler JNM-SD-HC was used for chemical shifts determination and integration. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external) where positive sign is downfield from the standard. All spectra were recorded on samples which consisted of the compound (ca 0.001 mol) in solvent (2 ml). IR spectra of samples were recorded on UR-10 (Zeiss), Intracord 137 (Perkin–Elmer) Spectrophotometers as thin films. Optical activity measurements were made with a Perkin–Elmer 141 photopolarimeter.

General preparative procedure for synthesis of alkyl thiocyanates and alkyl isothiocyanates (Table 2)

Method A. Chlorine (0.1 mol) was added with efficient stirring to a solution of an alkyl 1,2-phenylene phosphite (0.1 mol) in dry CH_2Cl_2 (100 ml) at − 80°C. The mixture was stirred for 1 h at the

same temperature and then the small excess of lead thiocyanate (0.11 mol) was added at $-40°C$ to give the diisocyanatophosphorane 9 (ν_{NCS} 1975-1985 cm^{-1}). Stirring of the soln of 9 was continued for 2 h at ambient temperature. The precipitate (PbCl$_2$) was filtered off and solvent was evaporated *in vacuo*. Alkyl thiocyanates (MeSCN, EtSCN, Pr^{n}SCN) were purified by distillation from phosphoroisothiocyanidate whereas the others by silica gel chromatography. Pure products were obtained by redistillation under the conditions listed in the Table 2. The mixture of alkyl thiocyanate and alkyl isothiocyanate was separated by column chromatography on silica gel (100-200 mesh) using benzene as eluent.

Method A'. Into the soln of freshly prepared thiocyanogen[13] (0.11 mol) in CH$_2$Cl$_2$ (80 ml) at $-40°C$ was added dropwise with stirring the soln of the corresponding alkyl 1,2-phenylene phosphite or mixed anhydride (0.1 mol) in the same solvent (50 ml). Stirred for additional 1 h under the same conditions to give the desired diisothiocyanatophosphorane with a quantitative yield. The soln of phosphorane was allowed to warm to room temperature, kept at room temperature for 1 h and concentrated *in vacuo*. The residual alkyl thiocyanate (RSCN) or acylisothiocyanate (RC(O)NCS), or phosphoroisothiocyanidate ($>$P(O)NCS) as well as the mixture of alkyl thiocyanate and alkyl isothiocyanate were separated and purified in the manner as described in method A.

Method B. Into the soln of triphenylphosphite (0.1 mol) in CH$_2$Cl$_2$ (100 ml) an equivalent amount of chine (0.1 mol) was added dropwise with stirring at $-40°C$. To this mixture lead thiocyanate (0.12 mol) was added under the same conditions to give a desired isothiocyanatophosphonium salt 8. A solution of appropriate alcohol or mixed anhydride (0.1 mol) in CH$_2$Cl$_2$ (10 ml) was added to a freshly prepared salt 8 at $-30°C$ and then the reaction mixture was stirred in the same temperature for 2 h. Lead chloride was filtered off and the residue was kept at room temperature overnight. The solvent was evaporated *in vacuo* and the residual alkyl thiocyanate, acylisothiocyanate, phosphoroisothiocyanidate and the mixture of alkyl thiocyanate and alkyl isothiocyanate were separated and purified as described in method A.

Method B'. Isothiiocyanatophosphonium salt 8 was prepared

by dropwise addition of triphenylphosphite (0.1 mol) in CH$_2$Cl$_2$ (50 ml) at $-40°C$ to a stirred solution of a freshly prepared thiocyanogen (0.11 mol) in the same solvent (80 ml). After the addition, the reaction mixture was stirred for 1 h at $-40°C$. Then a soln of appropriate alcohol or acid (0.1 mol) in CH$_2$Cl$_2$ (10 ml) was added dropwise at $-30°C$. The mixture was kept overnight at the room temperature. After evaporation of solvent *in vacuo*, the product was separated and purified as described in method A.

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