Novel Synthesis of Isothiocyanatophosphoranes and Isothiocyanatophosphonium Salts *via* Ligand Substitution. Versatile Reagents for Converting Hydroxy Groups into Thiocyanate and Isothiocyanate Functions

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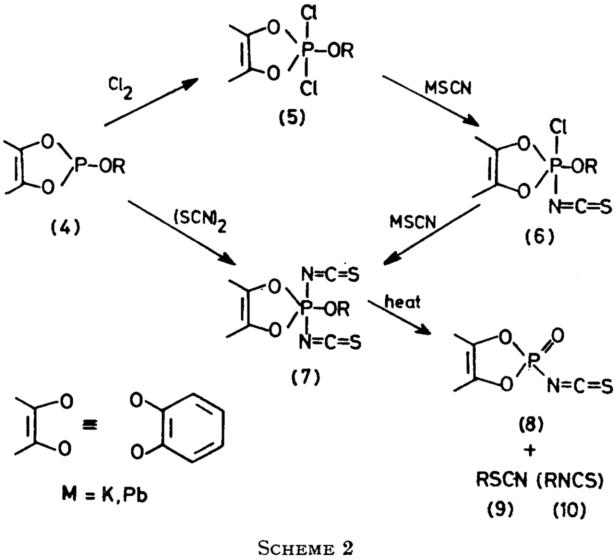
Summary Alkoxy- or acyloxy-isothiocyanatophosphoranes (**7**) and phosphonium salts (**12**), prepared under mild conditions by stepwise ligand substitution from (**5**) and (**11**), respectively, decompose in excellent yield into the corresponding thiocyanato (**9**) and isothiocyanato (**10**) derivatives, thus providing a new method of synthesis of (**9**) and (**10**).

WE have previously shown the possibility of preparation of organophosphorus compounds of the general formula $R^1_2R^2P(NCS)_2$ (**1**) by addition of thiocyanogen $(SCN)_2$ to three-co-ordinate phosphorus compounds $R^1_2R^2P$ (**2**) (Scheme 1).[1] Adducts of the type (**1**) decompose into alkyl thiocyanates R^3SCN or isothiocyanates R^3NCS when $R^2 = OR^3$.[1,2]

$$\begin{tikzcd}
\underset{(3)}{R^1_2R^2\,PCl_2} \arrow[r, "MSCN"] & R^1_2R^2P(NCS)Cl \arrow[d, "MSCN"] \\
\underset{(2)}{R^1_2R^2P} \arrow[r, "(SCN)_2"] & \underset{(1)}{R^1_2R^2P(NCS)_2}
\end{tikzcd}$$

SCHEME 1

We here report the synthesis of (**1**) *via* stepwise ligand substitution of the corresponding dichloro adducts $R^1_2R^2PCl_2$ (**3**) using a suitable metal thiocyanate. The application of this method is illustrated by Schemes 2 and 3 and the Table.



SCHEME 2

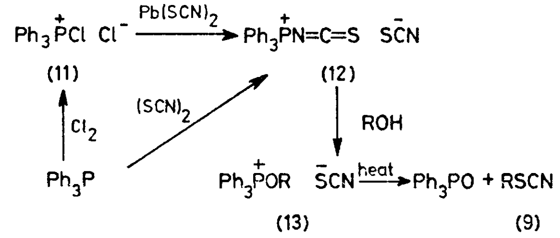
TABLE

Preparation of thiocyanato and isothiocyanato derivatives[a] from (**4**) and (**10**)

	(**4**)			(**10**)		
Alcohols and acids	Yield[b]/%	RSCN[c]/%	RNCS/%	Yield[b]/%	RSCN[c]/%	RNCS/%
MeOH	75	100	—			
EtOH	80	100	—	85	100	
Pr^nOH	84	99	—			
Bu^tCH_2OH	85	60	40	80	100	
$PhCH_2OH$	95	100	—	96	100	
Pr^iOH	80	95	5			
$MeCH(OH)[CH_2]_5Me$	85	78 $[\alpha]_D^{20} -31{\cdot}5°$	22 $[\alpha]_D^{20} -55{\cdot}5°$		91 $[\alpha]_D^{20} -45°$	9 $[\alpha]_D^{20} -56{\cdot}2°$
MeC(O)OH				50		100
$(EtO)_2P(O)OH$				55		100
$(EtO)_2P(S)OH$				55		100

[a] All products have i.r., n.m.r., and mass spectra consistent with the assigned structure. [b] Total yields of pure isolated compounds are based on the alcohols and acid used. [c] The percentage of RSCN and RNCS refer to their ratio in the products.

The chlorophosphoranes (**5**) prepared at −40 °C from (**4**) and elemental chlorine[3] were allowed to react with a small excess of potassium thiocyanate in methylene chloride in the presence of 18-crown-6 ether† at *ca.* −30 °C and gave (**7**) in quantitative yield‡ (R = Et; ^{31}P n.m.r. δ −77 p.p.m.; ν_{NCS} 1980 cm^{-1}). Interestingly it proves much easier to convert (**5**) into (**7**) by treatment with 20% excess of lead thiocyanate in absence of the crown ether under the same reaction conditions. Formation of the intermediate chloroisothiocyanatophosphoranes (**6**) was detected by ^{31}P n.m.r. spectroscopy [R=Et; $\delta(^{31}P)$ −54 p.p.m.]. When the phosphoranes (**7**) were warmed to ambient temperature they decomposed to the alkyl thiocyanates (**9**), when R=n-alkyl, and to a mixture of (**9**) and (**10**) when R = secondary alkyl group. Commercially available (**11**), which may also be prepared *in situ* from elemental chlorine and triphenylphosphine, has been converted under conditions described above into the phosphonium salt (**12**) [δ (^{31}P) +39 p.p.m.; ν_{NCS} 1990 cm^{-1}] in quantitative yield. A methylene chloride solution of (**12**) was allowed to react with the appropriate alcohol ROH at −30 °C to form the alkoxyphosphonium salts (**13**) [R=Et; δ (^{31}P) +61 p.p.m.].[4] The solution of (**13**) when warmed to ambient temperature gave (**9**) and (**10**) in excellent yield. The reaction of (**12**) with carboxylic acids and organic acids of phosphorus gave the corresponding acylisothiocyanates in good yields.



SCHEME 3

Control experiments indicated that the isothiocyanates (**10**) are not formed by the isomerisation (**9**)→(**10**) and their formation is related to the ambident character of the SCN^- anion. The methods discussed above can be applied to produce optically active (**9**) and (**10**).

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† 1,4,7,10,13,16-Hexaoxacyclo-octadecane; *ca.* 40% stocheiometric amount.

‡ Yields of reactive intermediates (**7**), (**12**), and (**13**) were estimated from the ^{31}P n.m.r. spectra; ^{31}P shifts are reported as positive downfield from 85% phosphoric acid as standard.

[1] E. Krawczyk, J. Michalski, M. Pakulski, and A. Skowrońska, *Tetrahedron Letters*, 1977, 2019.

[2] After ref. 1 on the adducts of thiocyanogen and three-co-ordinate phosphorus compounds was published, Tamura *et al.* used the adduct of thiocyanogen with triphenylphosphine in the synthesis of alkyl thiocyanates; T. Tamura, T. Kawaski, A. Adachi, M. Tanio, and Y. Kita, *Tetrahedron Letters*, 1977, 4417.

[3] A. Skowrońska, J. Mikołajczak, and J. Michalski, *J.C.S. Chem. Comm.*, 1975, 791.

[4] The generation of alkoxyphosphonium intermediates and their use in synthesis has been the subject of recent interest; *e.g.*: R. Appel, *Angew. Chem. Internat. Edn.*, 1975, **14**, 861; B. Castro and C. Selve, *Bull. Soc. chim. France*, 1971, 2296; G. Grynkiewicz and H. Burzyńska, *Tetrahedron*, 1976, 2109; K. S. Colle and E. S. Lewis, *J. Org. Chem.*, 1978, **4**, 571.