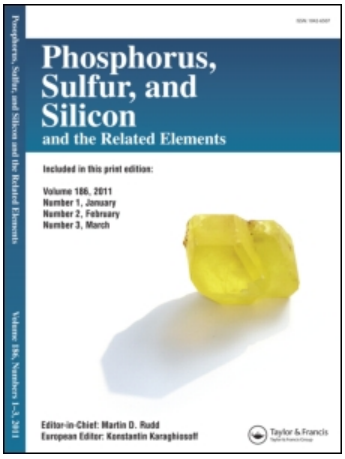

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REACTION OF BIS-[DIALKOXYPHOSPHORYL]- AND BIS-[DIALKOXYTHIOPHOSPHORYL]- DISULFIDES WITH TRIALKYLSILYLCYANIDES NEW ROUTE TO DIALKYLPHOSPHORO- AND DIALKYLTHIOPHOSPHORO THIOCYANIDATES AND O,O,O,O-TETRAALKYLPYROPHOS- PHOROTRITHIOATES

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REACTION OF BIS-[DIALKOXYPHOSPHORYL]- AND BIS-[DIALKOXYTHIOPHOSPHORYL]-DISULFIDES WITH TRIALKYLSILYLCYANIDES NEW ROUTE TO DIALKYLPHOSPHORO- AND DIALKYLTHIOPHOSPHORO THIOCYANIDATES AND O,O,O,O-TETRAALKYLPYROPHOSPHOROTRITHIOATES

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The reaction of organophosphorus disulfides with trialkylsilylcyanide has been investigated. It provided direct evidence for the intermediacy of thiocyanidate >P(X)SCN, X = O, S in this type of reaction. The disulfides studied involved phosphoryl, phosphonyl and/or phosphinyl disulfides. They have been shown to follow the common mechanism. The studied reaction of thiophosphoryl disulfides with trimethylsilylcyanide represents a new and highly efficient route to tetraalkylpyrophosphorotrithioates.

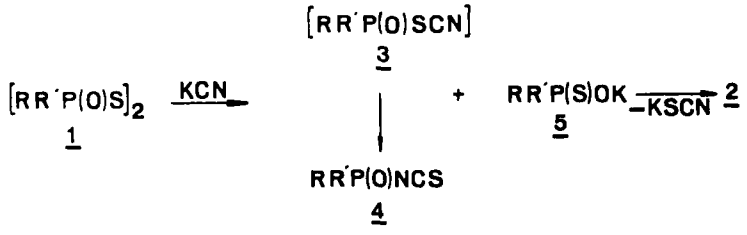
Organophosphorus disulfides of general formula $[(RO)_2P(X)S]_2$ (X = O, S) are relatively well known and readily available compounds.[2–4] They exhibit pseudohalogen properties typical for disulfides[5–10] and react smoothly with various nucleophiles with scission of the disulfide bond.[2,5,6,11,12]

In the earlier studies[13,14] it was demonstrated that the cleavage of the sulfur-sulfur bond in organophosphorus disulfides **1** by alkali cyanides leads to the formation of unsymmetrical monothiopyrophosphates **2** according to Equation 1.

$$\underset{\underline{1}}{RR'P(O)SS(O)PRR'} \xrightarrow[-MNCS]{MCN} \underset{\underline{2}}{RR'P(O)OP(S)RR'} \qquad (1)$$

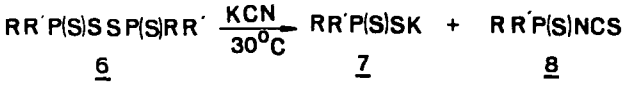
R = R' = Alkoxy
M = K, Na, NH_4, etc.

Our early investigation[15,16] of this reaction indicates that it follows a stepwise process. It probably involves the intermediate formation of the thiocyanidate >P(O)SCN **3** which undergoes further condensation with the salt of organophosphorus monothioic acid to form the thiopyrophosphate **2**. The bulky group attached to phosphorus may hinder the latter process and isomerisation of **3** → **4** catalysed by **5** is then observed as we have demonstrated earlier.[16,17] Interestingly, similar results were obtained in the reaction of bis-(dialkoxythiophosphoryl)disulfides **6**[16] (Equation 3). Supposedly, in this case the elevated temperature additionally favours the thiocyanidate-isothiocyanidate



R=R'=Alkoxy

rearrangement.[16,18] Our attempts to detect the intermediate formation of >P(X)SCN compounds in these reactions by IR and ^{31}P NMR spectroscopy failed.[16,17]

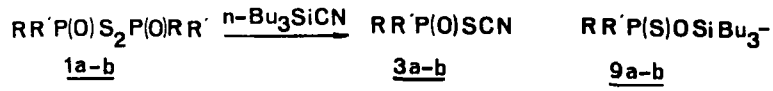


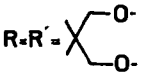
R=R'=Alkoxy

In this paper we would like to present our results on reactions of the bis-phosphoryl, phosphonyl, and phosphinyl as well as bis-thiophosphoryl disulfides with trialkylsilylcyanides. The use of this reagent as a cyanide source was expected to prevent the formation of $>P(S)X^-$ claimed previously responsible for extremely facile >P(X)SCN → >P(X)NCS rearrangement[16] and to allow us for the first time to proof directly the intermediacy of thiocyanidates >P(X)SCN in the cleavage reaction of organophosphorus disulfides by cyanide. Full characterisation of these elusive intermediates, including isolation in one case, and the novel highly efficient and operationally simple synthesis of tetraalkylpyrophosphorotrithioates **13** is described.

RESULTS

We have found that the tri-n-butylsilylcyanide reacts smoothly in dichloromethane with stoichiometric amounts of disulfides **1a–b** even at −30°C. The quantitative formation of two organophosphorus products the thiocyanidate **3a–b**



a) R=R'=Bu^tCH_2O–; b) R–R' = 

and O-tri-n-butylsilylthiophosphate **9a–b** was observed in these reactions as established by ^{31}P NMR spectroscopy. The ^{31}P NMR chemical shifts of **3a–b** and **9a–b** obtained in these reactions were identical with those found for the authentic samples obtained on the independent way.[19] The reaction seems to be general in

$$\underset{\underset{\text{c) } R'=C_6H_5-;\quad \text{d) } R'=CH_3O-;}{\underline{1c-d}}}{Bu^tR'P(O)S_2P(O)Bu^tR'} \xrightarrow{Me_3SiCN} \underset{\underline{3c-d}}{R'Bu^tP(O)SCN} + \underset{\underline{10c-d}}{R'Bu^tP(S)OSiMe_3} \quad (5)$$

scope since other disulfides **1c, d** derived from thiophosphinic and thiophosphonic acids may be used to obtain the corresponding thiocyanidates **3c, d** in reaction with trimethylsilylcyanide. Some examples are shown in Equation 5. All thiocyanidates **3a–d** appear to be stable in solution and their rearrangement into the isomeric isothiocyanidates **4** was not observed under the reaction conditions (see Table I). In one favourable case O-methyl t-butylphosphonothiocyanidate (**3d**) was separated from the reaction mixture by distillation. Attempts to purify thiocyanidate **3a–c** by distillation or crystallisation failed and lead exclusively to isolation of the corresponding isothiocyanidates **4a–c** (Table I).

$$\underset{\underline{3\,a-c}}{RR'P(O)SCN} \xrightarrow{\Delta,\ \text{distill.}} \underset{\underline{4\,a-c}}{RR'P(O)NCS} \quad (6)$$

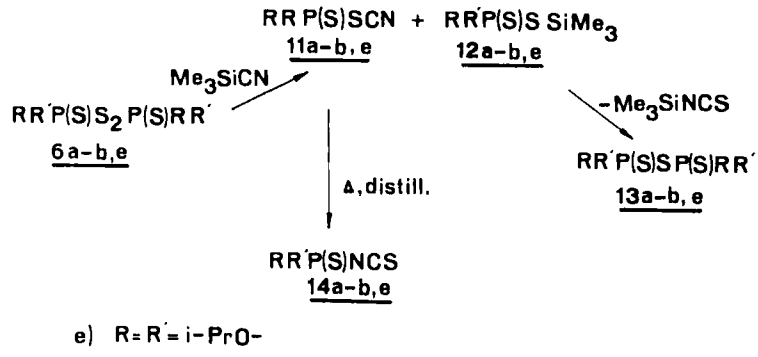
In order to get further insight into the studied process a model reaction between **1a** and Me_3SiCN in CH_2Cl_2 was monitored by means of low temperature ^{31}P NMR spectroscopy. At $-60°C$ only one line at $\delta + 20.0$ characteristic of starting disulfide **1a** was observed. At the temperatures near $-40°C$ two new

TABLE I

Characterisation of products of the reaction of **1a–d** with R''_3SiCN

R	R′	R″	^{31}P NMR ppm **3**	^{31}P NMR ppm b.p. (m.p.) (°C) elemental anal. Yield **4**	**9**
Bu^tCH_2O	Bu^tCH_2O	n-Bu	**3a**, +10.4	**4a**, −18.2; b.p. 76–78/0.1 mmHg Lit.[16] ^{31}P NMR −18.5 Calcd.: C, 47.30; H, 7.93; N, 5.01; P, 11.8; S, 11.53 Found: C, 49.86; H, 7.66; N, 5.47; P, 8.95; S, 11.53; 85%	**9a**, +55.3; b.p. 88–89/0.1 mmHg Calcd.: C, 49.67; H, 9.22; P, 9.14; S, 9.47 Found: C, 50.01; H, 10.06; P, 8.21; S, 8.57; 85%
		n-Bu	**3b**, +0.6	**4a**, −25.8; m.p. 77–78 Calcd.: C, 34.78; H, 4.86; N, 6.76; P, 14.95; S, 15.47 Found: C, 35.80; H, 5.14; N, 6.21; P, 15.26; S, 14.35 96%	**9b**, +49.7; b.p. 170/0.05 mmHg; Calcd.: C, 53.65; H, 9.80; P, 8.14; S, 8.44 Found: C, 54.47; H, 10.11; P, 7.51; S, 8.68 85%
Bu^t	Ph	Me	**3c**, +73.0	**4c**, +39.0; b.p. 94–97/0.1 mmHg (Lit.[17] ^{31}P NMR +39.6) 88%	**10c**, +93.0; b.p. 90/0.05 mmHg 80%
Bu^t	MeO	Me	**3d**, +62.3		**10d**, b.p. 58–60/0.1 mmHg Calcd.: C, 39.67; H, 8.80; P, 12.88 Found: C, 39.63; H, 8.80; P, 12.50

SCHEME I



e) R = R' = i-PrO-

signals in the neighbourhood of substrate **1a** were observed: the line at $\delta + 10.2$ for thiocyanidate **3a** and at $\delta + 55.6$ for the silylester $(Bu^tCH_2O)_2P(S)OSiMe_3$ (**10a**). After 30 min. at the temperatures −30°C to −25°C the reaction was completed and only two lines of the final products **3a** and **10a** were observed.

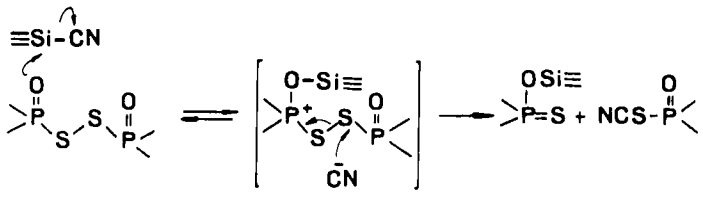
The bis-(dialkoxythiophosphoryl)disulfides **6a–b, e** follow a similar pattern in their reaction with trimethylsilylcyanide. The reactions are, however, considerably slower and require several hours at room temperature for completion. Two major products were identified by ^{31}P NMR spectroscopy in each of the studied cases i.e. the thiocyanidate **11a–b, e** and O,O-dialkyl-S-trimethylsilylphosphorodithioate **12a–b, e** formed in 20–25% yield (1:1 ratio) and only 5–8% of pyrophosphorotrithioate **13** (see Table II). As observed previously for oxy analogs **3a–c** distillation of the reaction mixture at this stage leads to the isolation of the corresponding isomerized products **14a–b, e** and esters **12a–b, e** (Table II). When the reactions are continued for additional 4–10 days the formation of only one product pyrophosphorotrithioate **13a–b, e** results. Evaporation of solvent and trimethylsilylisothiocyanate in vacuo leaves crude **13** which after crystallisation or

TABLE II

Characterisation of products of the reaction of **6a, b, e** with Me_3SiCN

R	R'	^{31}P NMR ppm **11**	^{31}P NMR ppm b.p. (m.p.) (°C) elemental anal. **14**	**12**	**13**
Bu^tCH_2O	Bu^tCH_2O	**11a**, +72.7	**14a**, +46.3; b.p. 71/0.05 mmHg Calcd.: C, 44.72; H, 7.50; N, 4.73; P, 10.48; S, 21.70; Found: C, 44.98; H, 7.51; N, 4.77; P, 10.40; S, 20.18	**12a**, +89.2; b.p. 78/0.01 mmHg	**13a**, +79.0; b.p. 144/0.05 mmHg
		**11b**, +65.5	**14b**, +36.6; m.p. 80–81 Calcd.: C, 35.74; H, 4.28; N, 5.95; P, 13.17; S, 27.26 Found: C, 32.47; H, 4.74; N, 5.78; P, 14.12; S, 29.80	**12b**, +80.0; b.p. 97/0.01 mmHg	**13b**, +65.5; m.p. 247–248
i-PrO	i-PrO	**11e**, +69.0	**14e**, +21.0; b.p. 63–64/ 0.18 mmHg	**12e**, +86.0; b.p. 68/0.01 mmHg	**13e**, +75.0; b.p. 105/0.01 mmHg

distillation provides pure product in nearly quantitative yield. This can therefore be considered as a convenient and highly efficient route to **13**.[20]

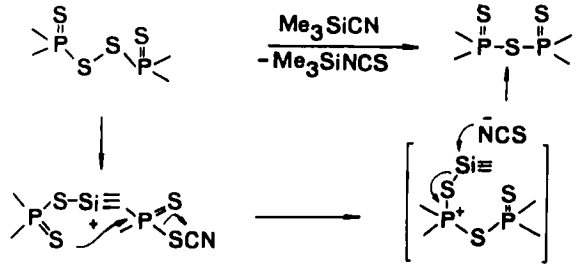


(7)

15

The success of the presented approach in detecting and isolating the intermediate >P(X)SCN compounds in the reaction of organophosphorus disulfides with cyanide is apparently due to the lack of any nucleophilic reagents or impurities in the reaction medium. It allowed us to clarify the detailed sequence of events in this type of transformation. It seems most probable that in the first step of the reaction (Equation 4), the attack of the phosphoryl oxygen atom of the disulfide on the silylcyanide takes place. As a result, the phosphonium salt **15** is formed. The subsequent fast attack of the CN^- anion on the sulfur atom causes the scission of the disulfide bond and formation of the final products ensues. The detection of such apparently short-lived intermediates **15** by low temperature ^{31}P NMR spectroscopy appeared not to be possible. The discussed mechanistic scheme (Equation 7) agrees well with the known pattern of reactivity of the esters of phosphoric, phosphorothioic, and phosphoroselenoic acids[21] towards organosilicon halides as well as nucleophilic displacement at sulfenyl sulfur.[8,9] Apparently, the same mechanistic scheme can be applied to the reaction of bis-(dialkoxythiophosphoryl)disulfide **6** with trimethylsilylcyanide though in this case, the reaction is expected to be considerably slower due to the lower affinity of sulfur to silicon. Finally, the reaction of disulfides **6** with silylcyanide can be considered as an overall desulfurization process (Scheme II) resulting in trithiopyrophosphate **13** formation. The remarkable facility of this process renders it a convenient and highly efficient route to O,O,O-tetraalkylpyrophosphorotrithioate. The origin of this facility can be ascribed to the favourable bond energetics (≡Si—N vs ≡Si—S) and the pronounced leaving ability of —SCN group in organophosphorus thiocyanidate.

SCHEME II



EXPERIMENTAL

The solvent and reagents were purified by conventional methods. ^{1}H NMR spectra were recorded on a Jeol-INM 60 HL and Perkin–Elmer R12B instruments. ^{31}P NMR spectra were measured with INM-FX60 FT spectrometer with 85% H_3PO_4 as internal standard. The negative values correspond to compounds absorbing at higher field than H_3PO_4. IR spectra of samples were recorded on Infracord 137 Perkin–Elmer and Specord 71 Zeiss spectrometers. The synthesis of disulfides **1a**, **1c**,[16] **1b** (m.p. 140–141°C, ^{31}P NMR 11.8 ($CHCl_3$); lit.[22] m.p. 129°C), **6e**[23] were described. The preparation of other disulfides were performed by oxidation of potassium O-methyl-t-butylphosphonothioate with iodine, **1d**; dineopentylphosphorodithioic acid with bromine, **6a**; potassium salt of 5,5-dimethyl-2-thiono-2-mercapto-1,3,2-dioxaphosphorinane with iodine, **6b**.

Bis-(O-methyl-t-butylphosphonyl)disulfide **1d**. White prisms, m.p. 78–82°C, ^{1}H NMR(CCl_4) δ_{Bu^t} 1.225; 1.275 (18H, t.d) $^3J_{HCCP}$ 16.5 Hz, δ_{CH_3O} 3.925; 3.825 (6H, t.d) $^3J_{HCOP}$ ^{12} Hz (Found: C, 36.1; H, 7.1; P, 19.3; $C_{10}H_{24}O_4P_2S_2$ requires C, 35.9; H, 7.23; P, 18.4).

Bis-(O,O-2,2-dimethylpropylthiophosphoryl)disulfide **6a**. Pale yellow prisms m.p. 71–73°C; ^{31}P NMR δ 84.4 (CH_2Cl_2); (Found: C, 44.35; H, 8.15; P, 11.0; $C_{20}H_{44}O_4P_2S_4$ requires C, 44.58; H, 8.23; P, 11.49; S, 23.80).

Bis-(5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl)disulfide **6b**. Prisms m.p. 141–142°C, ^{31}P NMR δ 79.3 (CH_2Cl_2) (Found: C, 30.78; H, 5.10; P, 16.67; S, 32.34; $C_{10}H_{20}O_4P_2S_4$ requires C, 30.44; H, 5.11; P, 15.70; S, 32.51).

The reaction of **1a–d** *with trialkylsilylcyanide (general procedure)*. To the solution of disulfide (0.01 mole) in dry CH_2Cl_2 10–20 ml, was added with stirring at temperature of −15°C 0.011 mole of R_3SiCN (R = n-Bu or Me). The stirring was continued for the next 1 to 15 hr at room temperature and the reaction mixture was analysed by ^{31}P NMR spectroscopy. The ^{31}P chemical shift values of formed thiocyanidates **3a–d** and silylesters **9a–b**, **10c–d**, are given in Table I. After the subsequent evaporation of the solvent and fractional distillation of residual liquid in vacuo the isothiocyanidate **4a–c** and esters **9a, b**, **10c–d** were obtained (Table I).

The reaction of Me_3SiCN with disulfide **1d**. Into the stirred solution of 10.9 g (0.03 mole) of disulfide **1d** in 30 ml dry CH_2Cl_2 was added dropwise 3.0 g (0.03 mole) of freshly prepared Me_3SiCN in of 5 ml CH_2Cl_2 at 15°C. The stirring was continued for the next 35 min. at 15°C. The solvent was evaporated at 10–15°C/10 mmHg and the residual liquid was fractionated under high vacuum. Two fractions were obtained a) b.p. 49–50/0.05 mmHg, IR 2174 (−SCN) 1273 (P = O) ^{31}P NMR δ 62.3 (CH_2Cl_2) identified as O-methyl t-butylphosphonothiocyanidate (**3d**), yield 3.9 g (68%): b) b.p. 58–60/0.1 mmHg ^{31}P NMR δ 97.7 (CH_2Cl_2) (Found: C, 39.63; H, 8.30; P, 12.5; $C_8H_{21}O_2PSSi$ requires C, 39.97; H, 8.80; P, 12.88;) identified as a **10d**.

The reaction of Me_3SiCN with **6a, b, e** (Table II). Into the stirred solution of 0.01–0.05 mole of disulfide **6a, b, e** in 15–40 ml of dry CH_2Cl_2 the 0.011–0.052 mole of Me_3SiCN was added at 15–20°C. The resulting solution was stirred at 20° for 8–12 hr. After this time the presence of thiocyanidate **11a, b, e**, silylesters **12a, b, e** (ratio 1:1; yield 20–25%) 5–8% **13a, b, e** and starting **6a, b, e** was observed by ^{31}P NMR.

The reaction of **1a** *with Me_3SiCN (^{31}P NMR low temp. analysis).* To the solution of 0.25 g **1a** in 2 ml of CH_2Cl_2 placed in 10 mm NMR tube 0.051 g of Me_3SiCN was added by syringe and the reaction course followed by ^{31}P NMR spectroscopy at the time intervals and temperatures raising from −60°C to −25°C.

The synthesis of O,O,O,O-tetraalkyltrithiopyrophosphates O,O,O,O-tetra(2,2-*dimethylpropylpyrophosphorotrithioate* (**13a**).

The mixture of 5.38 g (0.01 mole) of **6a** and 1.1 g (0.011 mole) of Me_3SiCN in 25 ml of CH_2Cl_2 was stirred for 8 days at 18–20°C. The solvent and Me_3SiNCS was distilled off. The residual oily liquid was purified by distillation. Pale yellow oil b.p. 144–145°C/0.05 mmHg (yield 4.7 g, 93%); ^{31}P NMR +79 (neat) (Found: C, 47.50; H, 8.81; P, 12.10; $C_{20}H_{44}O_4P_2S_3$ requires C, 47.40; H, 8.75; P, 12.22).

O,O,O,O-tetraisopropylpyrophosphorotrithioate (**13e**). The solution of 3.17 g (0.032 mole) of Me_3SiCN and 12.79 g (0.03 mole) of disulfide **6e** in 30 ml of CH_2Cl_2 was stirred at 20–22° for 6 days. The fractional distillation of the reaction mixture gave **13e** as a oily liquid b.p. 105–107°C/0.01 mmHg (lit.[14] b.p. 105–108°C/0.01 mmHg) (yield 10.7 g, 91%); ^{31}P NMR δ 75.0 (neat); (Found: C, 36.48; H, 7.09; P, 15.80; $C_{12}H_{28}O_4P_2S_3$ requires C, 36.53; H, 7.15; P, 15.70).

Bis-(5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl)sulfide (**13b**). The solution of 1.97 g (0.005 mole) of **6b** and 0.51 g (0.0052 mole) of Me_3SiCN in 30 ml of dry CH_2Cl_2 was stirred for 10 days at room temperature. The solvent and volatile products were distilled off and a residual solid was purified by crystallisation from CH_3CN. **13b** was obtained in colourless prisms m.p. 247–248°C, ^{31}P NMR δ 65.5 (CH_3CN); (yield 1.73 g, 96%); (Found: C, 33.19; H, 5.57; P, 17.27; S, 25.76; $C_{10}H_{20}O_4P_2S_3$ requires C, 33.14; H, 5.56; P, 17.09; S, 26.54).

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