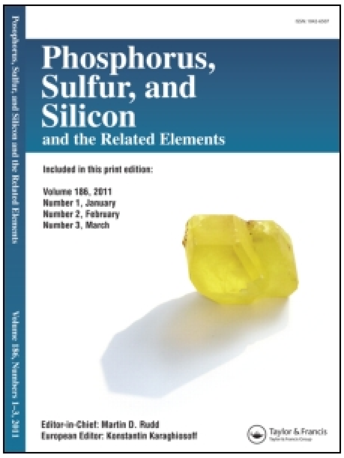

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A NEW SYNTHESIS OF BIS-PHOSPHORYL DISULFIDES$[(RO)_2 P(O)S]_2$

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A NEW SYNTHESIS OF BIS-PHOSPHORYL DISULFIDES $[(RO)_2P(O)S]_2$

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Bis-phosphoryl disulfides **2** are synthesized in excellent yields from the phosphorothiorates **5** by means of half equimolar amounts of sulfuryl chloride. In the case of cyclic diastereoisomeric phosphorothioates derivatives of 4-methyl-1,3,2-dioxaphosphorinan, the pronounced kinetic preference of exocyclic axial sulfur atoms towards disulfides bond formation have been demonstrated.

The bis-phosphoryl disulfides **2** play an important role in the synthesis of organophosphorus-sulfur compounds[1] because of their pronounced pseudohalogen type reactivity.

The formation of **2** by oxidation of the corresponding phosphorothioic acids salts **1** in aqueous medium with elemental iodine has already been reported in 1945 by O. Foss.[2]

$$\underset{\mathbf{1}}{2(RO)_2P(S)O^-} \xrightleftharpoons{I_2} \underset{\mathbf{2}}{[(RO)_2P(O)S]_2} + 2I^- \quad (1)$$

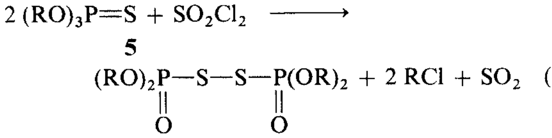
More recently the disulfides **2** have been obtained in our laboratory[3] in anhydrous medium by the condensation of oxophosphoranesulfenyl chlorides **3** with phosphorothioic acids **4**

$$\underset{\mathbf{3}}{(RO)_2P(O)SCl} + \underset{\mathbf{4}}{HO(S)P(OR'')_2} \longrightarrow \mathbf{2} + HCl \quad (2)$$

or by the chlorination of monothioacids **4** with sulfuryl chloride or elemental chlorine.

$$2\,\mathbf{4} + SO_2Cl_2 \longrightarrow \mathbf{2} + 2\,HCl + SO_2 \quad (3)$$

In this paper we wish to describe a convenient route to the bis-phosphoryl disulfides **2** involving the reaction of trialkylphosphorothioates with half molar equivalents of sulfuryl chloride.



$$\underset{\mathbf{5}}{2\,(RO)_3P{=}S} + SO_2Cl_2 \longrightarrow (RO)_2\underset{O}{\underset{\|}{P}}{-}S{-}S{-}\underset{O}{\underset{\|}{P}}(OR)_2 + 2\,RCl + SO_2 \quad (A)$$

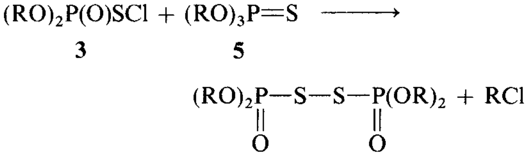
2

The reaction is very simple and takes place in non polar solvents below or slightly above room temperature depending on the structure of **5**. The yield is near quantitative and the products, after removal of solvent in vacuo, are, according to ^{31}P NMR spectroscopy, of high purity and can be used directly for other synthetic procedures without any further purification. The removal of solvent is often not necessary. Yields, physical and spectral data for the disulfides **2** are summarised in the Table.

We found earlier[4] that thionophosphates **5** form oxophosphoranesulfenyl chlorides **3** when reacted with elemental chlorine or sulfuryl chloride in quantitative yields.

$$\mathbf{5} + SO_2Cl_2 \longrightarrow \mathbf{3} + RCl + SO_2 \quad (4)$$

We have now verified that the oxophosphoranesulfenyl chlorides **3** react with the thionophosphates **5** to yield the disulfides **2**[5]



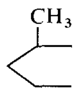
$$\underset{\mathbf{3}}{(RO)_2P(O)SCl} + \underset{\mathbf{5}}{(RO)_3P{=}S} \longrightarrow (RO)_2\underset{O}{\underset{\|}{P}}{-}S{-}S{-}\underset{O}{\underset{\|}{P}}(OR)_2 + RCl \quad (B)$$

2

Therefore, it may be concluded that reaction (A) proceeds via the initial formation of oxophosphoranesulfenyl chloride **3** from the thionophosphate **5**. Subsequently the phosphonium salt **6** is formed by nucleophilic attack of the thionophosphate sulfur atom on the sulfenyl chloride

TABLE I

Preparation of bis-phosphoryl disulfides **2** from phosphorothioates **5** and sulfuryl chloride

Product No.	R	Route	Reaction time	Yield[a] [%]	Molecular[b] formula	$n_D^{20^\circ}$ [c]	^{31}P-NMR δ [ppm]	^{1}H-NMR ($CDCl_3$) δ [ppm]	IR (nujol) ν_{max}[cm^{-1}]
2a	CH_3	A B	2.5 h 2.0 h	95 90	$C_4H_{12}O_6P_2S_2$ (282.2)	1.4966 (1.4968)	23.5	3.83[d] (d, 12H, CH_3 $^3J_{POCH}$ = 13.2 Hz)	1256 (P=O) 530 (P—S—)
2b	C_2H_5	A B	3.0 h 3.0 h	100 95	$C_8H_{20}O_6P_2S_2$ (338.3)	1.4853 (1.4866)	19.9	1.3[d] (t, 12H, CH_3 $^3J_{HCCH}$ = 6.8 Hz) 4.2 (dq, 8H, CH_2 $^3J_{POCH}$ = 8.8 Hz)	1252 (P=O) 535 (P—S—)
2c	i-C_3H_7	A B	6.0 h 5.0 h	92 87	$C_{12}H_{28}O_6P_2S_2$ (394.4)	1.4671 (1.4761)	17.2	1.4[e] (d, 24H, CH_3 $^3J_{HCCH}$ = 6.4 Hz) 4.8 (dsep, 4H, —CH $^3J_{POCH}$ = 14.6 Hz)	1270 (P=O) 555 (P—S—)
2d	n-C_4H_9	A	7.0 h	85	$C_{16}H_{36}O_6P_2S_2$ (450.5)	1.4763 (1.4770)	20.3	0.9[d] (t, 12H, CH_3 $^3J_{HCCH}$ = 5.8 Hz) 1.5 (m, 16H, CH_2) 4.05 (dt, 8H, —CH_2—O— $^3J_{POCH}$ = 8.4 Hz)	1300 (P=O) 525 (P—S—)
2f	 CH$_3$ trans, trans (96% d.p.)	A B	20 min 10 min	100 92	$C_8H_{16}O_6P_2S_2$ (334.3)	1.5303	11.4	1.1[e] (dd, 6H, CH_3 $^3J_{HCCH}$ = 6 Hz, $^4J_{POCH}$ = 2.4 Hz) 4.2 (m, 10H, CH, CH_2)	1280 (P=O) 540 (P—S—)

[a] Estimated by ^{31} P-NMR analysis.

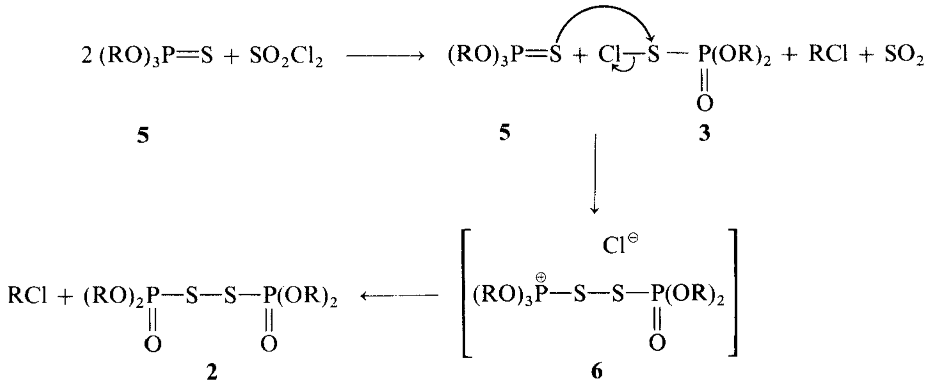
[b] All products gave satisfactory microanalyses (C ± 0.6; H ± 0.2; P ± 0.7; S ± 0.8).

[c] In parenthesis are given lit. values.[3,11]

[d] Measured with a Jeol spectrometer.

[e] Measured with a Tesla spectrometer.

sulfur atom. Finally, dealkylation affords the disulfide **2** as shown below:



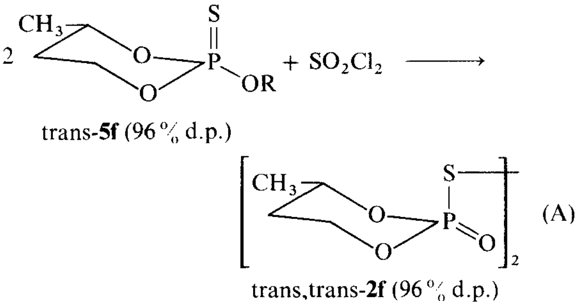
$$2\,(RO)_3P{=}S + SO_2Cl_2 \longrightarrow (RO)_3P{=}S + Cl{-}S{-}\underset{\underset{O}{\|}}{P}(OR)_2 + RCl + SO_2$$

$$\left[(RO)_3\overset{\oplus}{P}{-}S{-}S{-}\underset{\underset{O}{\|}}{P}(OR)_2 \quad Cl^{\ominus}\right] \longrightarrow RCl + (RO)_2\underset{\underset{O}{\|}}{P}{-}S{-}S{-}\underset{\underset{O}{\|}}{P}(OR)_2$$

5 **5** **3** **6** **2**

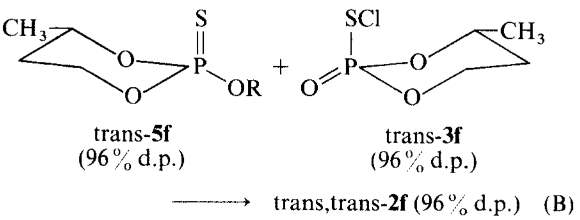
It was not possible to detect in this case the phosphonium salt **6**. This infers that the reaction between **3** and **5** leading to **6** is distinctly slower than the dealkylation of **6**.

Routes (A) and (B) have also been investigated with the aid of diastereoisomeric cyclic thionophosphates cis-**5e** and trans-**5f** and cyclic oxophosphoranesulfenyl chlorides cis-**3e** and trans-**3f**. It is noteworthy to mention the pronounced kinetic preference of exocyclic axial sulfur atoms towards disulfide bond formation. For example the reaction of trans - 2 - methoxy - 2 - thio - 4 - methyl - 1,3,2 - dioxaphosphorinane **5f** with sulfuryl chloride and the reaction of **5f** with trans-2-chlorothio-2-oxo-4 - methyl - 1,3,2 - dioxaphosphorinane **3f** proceed readily at −20°C in contrast to that of cis-2-chlorothio - 2 - oxo - 4 - methyl - 1,3,2 - dioxaphosphorinane **3e** with sulfuryl chloride and between *cis*-**5e** and cis-**3e** and trans-**5f** and cis-**3e**, which require much more drastic conditions. The configuration of cis-**5e** and trans-**5f** has been well established.[6] The stereoselective synthesis and assignment of the cis- and trans-configuration of cyclic oxophosphorane sulfenyl chlorides **3e** and **3f** were reported from this laboratory.[7] The disulfide **2f** formed from trans-**5f** in reaction (A) and from trans-**5f** and trans-**3f** in reaction (B) most likely has the trans, trans configuration which follows from ^{31}P NMR results. Characteristic splitting patterns are found in other trans isomer derivatives of 4 methyl 1,3,2 dioxaphosphorinans too.[7,8] The trans, trans configuration of **2f** was corroborated by the reaction where the disulfide **2f** was transformed by the action of sulfuryl chloride into trans-**5f**.



trans-**5f** (96% d.p.)

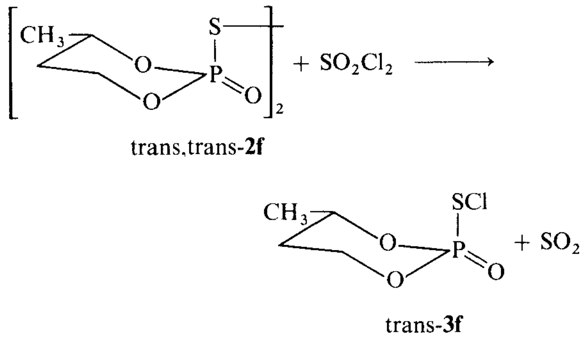
trans,trans-**2f** (96% d.p.)



trans-**5f** (96% d.p.)

trans-**3f** (96% d.p.)

⟶ trans,trans-**2f** (96% d.p.) (B)



trans,trans-**2f**

trans-**3f**

The reaction of cis-**5e** with sulfuryl chloride led to a mixture of diastereoisomeric disulfides. Similar results are obtained in the reaction between **5f** and **3e** and between **5e** and **3e**.

EXPERIMENTAL

Solvent were purified by conventional method. ^1H-NMR spectra were recorded on a Tesla BS-487C 80MHz spectrometer or Jeol JNM-C-60HL 60 MHz spectrometer using

Me_4Si as an internal standard. ^{31}P-NMR spectra were obtained on a Jeol JNM-C-60HL instrument at 24.3 MHz with external H_3PO_4 as a reference. Positive chemical shift values are reported for compounds absorbing at lower fields than H_3PO_4. The IR spectra were recorded on a Specord 71 IR (C. Zeiss) spectrophotometer. Products purities were determined from integrated ^{31}P-NMR spectra and TLC [Silufol UV 254 plates, benzene-acetone-chloroform (20:10:3); iodine vapour as developer] analysis.

Trialkyl phosphorothioates were prepared from thiophosphoryl chloride and the appropriate alkoxides.[9] *Cis- and trans-2-methoxy-2-thiono-4-methyl-1,3,2-dioxaphosphorinanes* were obtained by addition of elemental sulfur to the corresponding tri-co-ordinate phosphorus compounds at 5°C in benzene.

Dialkoxyoxophosphoranesulfenyl chlorides and *cis-* and *trans-2-chlorothio-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes* were synthesized according to the procedure described by Michalski and Skowronska.[4,7]

Bis-Phosphoryl Disulfides. General Procedure, Route A

A mixture of sulfuryl chloride (10 mmol) and corresponding trialkyl phosphorothioate (20 mmol) in methylene chloride (30 ml) was stirred at room temperature.[10] The reaction progress was monitored by TLC. After completion of the reaction, solvent and volatile products were removed under reduced pressure. In the synthesis of compounds **2c**, **2d** a slight excess of SO_2Cl_2 was used and the resulting mixture subsequently washed with aqueous solution of K_2CO_3 and water. The organic layer was dried over $MgSO_4$ and evaporated to give virtually pure disulfide **2** as evidenced by IR, NMR spectroscopy and TLC analysis.

Route B

To a solution of phosphorothioate (20 mmol) in methylene chloride (20 ml) a solution of crude oxophosphoranesulfenyl chloride in methylene chloride (20 ml) was added at 5°C. The mixture was stirred at room temperature.[10] The reaction progress was monitored by TLC. Upon completion, solvent and volatile products were removed under reduced pressure.

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