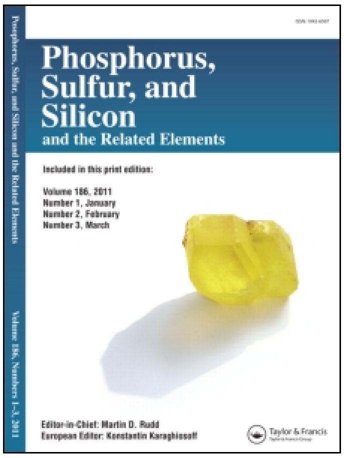

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SYNTHESIS OF 1,3,2-OXATHIAPHOSPHOLANE-2-SULFIDE DERIVATIVES

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SYNTHESIS OF 1,3,2-OXATHIAPHOSPHOLANE-2-SULFIDE DERIVATIVES

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5-substituted 2-alkyl (or aryl, heteroaryl, ...)thio-1,3,2-oxathiaphospholane-2-sulfides **5** are readily accessible by reaction of the triethylammonium salt **1** of a diester of the phosphorotetrathioic acid with appropriate epoxides in the presence of BF_3/Et_2O as catalyst.

Key words: BF_3/Et_2O; cyclisation reaction; NMR; oxathiaphospholane derivatives; oxiranes; phosphorotetrathioic acid; triethylammonium salts.

INTRODUCTION

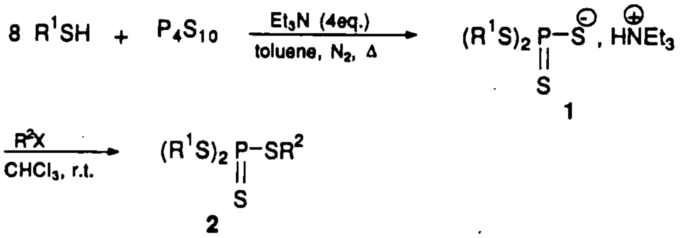
Some unsymmetrical triesters of the phosphorotetrathioic acid are known for their biological properties as well as their weaker toxicity compared to the oxygen analogues.[1] The synthesis of these compounds is accomplished by reacting a thiol with phosphorus pentasulfide[2] or phosphorus thiochloride.[3] In both cases, the crucial step is the purification of the mono or diester of the phosphorotetrathioic acid (or its chloride).

Recently we have described[4] a synthesis of unsymmetrical triesters of phosphorotetrathioic acid **2** based on the formation of the triethylammonium salt **1** of a diester of phosphorotetrathioic acid. These salts are stable and relatively easy to purify. The condensation of **1** with various halides leads to the desired unsymmetrical triesters **2** (see Scheme I).

We have given our attention now to the reactivity of the intermediate salts **1**.

RESULTS AND DISCUSSION

While the O,O-diesters of the phosphorodithioic acid **3** add easily to epoxides to give the phosphorus and sulfur containing alcohols **4**,[5] no similar reaction occurs



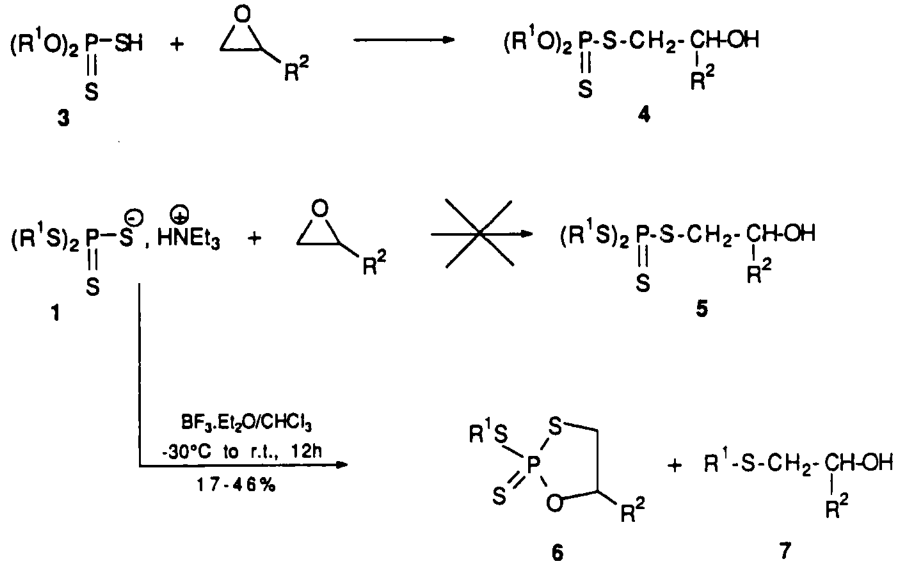
SCHEME I

with the salts **1**. On the other hand, the use of a Lewis acid (BF_3/Et_2O) as catalyst doesn't lead to the formation of the analogous alcohols **5** but to 2-alkyl (or aryl, ...) thio-1,3,2-oxathiaphospholane-2-sulfides **6** and 2-mercaptoethanol derivatives **7** coming from addition of the thiol, released by the formation of **6**, to the epoxide (see Scheme II).

We suppose that the formation of **6** is due to a reaction of the alkoxide, formed by opening the epoxide, on the phosphorus atom in **1**. The great affinity of phosphorus for oxygen and the proximity of both atoms in the supposed intermediate can explain the unexpected formation of the cyclic compound **6**.

The reaction is run in freshly distilled chloroform under an inert gas atmosphere (N_2). A great excess of epoxide (10 eq.) is added to a solution of **1** (1 eq. in chloroform) at −30°C followed later by 0,2 eq. of the Lewis acid at the same temperature. At that temperature the formation of the 2-mercaptoethanol derivatives **7** is reduced, even avoided in some cases. The exothermal reaction on addition of the Lewis acid favours the decomposition leading to **7**. Working at low temperature is therefore necessary. A large amount of phosphorus containing oligomers is also formed during the formation of **6**, which explains the moderate yields obtained.

^{13}C NMR of the isolated product **6d–g** shows 2 separate signals for the methyl group. These signals are separated by 10 to 11 Hz (see Table I) which is too high



6	R¹	R²	6	R¹	R²
a	Et	H	**e**	Ph	CH_3
b	Ph-CH_2	H	**f**	Ph-CH_2	CH_3
c	Furfuryl	H	**g**	Furfuryl	CH_3
d	Et	CH_3			

SCHEME II

for a $^3J_{C-P}$ coupling constant. These two peaks must therefore be assigned to two different methyl groups. This can be seen by ^{13}C NMR using a SEFT pulse sequence.

On the other hand, we observed that this reaction is regiospecific, the salt **1** adding only on the less hindered carbon atom of the epoxide. Thus only one signal appears in the ^{31}P NMR spectra (see Table I).

In summary we present here a new and easy two-step route to 2-alkyl (or aryl, ...)thio-1,3,2-oxathiaphospholane-2-sulfides substituted or not at the 5-position. Very few of them are known and they have been prepared usually by other methods[6,7] or by reaction of the salts **1** with β-bromo alcohols.[8]

Although the yields are sometimes modest, this is overcome somewhat by the easy availability of the starting materials and by the simplicity of the process.

TABLE I

Physical and spectral data of compounds **6a–g**

Product	Yield [a] (%)	mp (°C)	Molecular Formula	^{1}H-NMR [b, d] (60 MHz, $CDCl_3$/TMS) δ, $^3J_{P-H}$ (Hz)	^{13}C-NMR [b, e] (20.1 MHz, $CDCl_3$) δ, J_{P-C}(Hz)	^{31}P-NMR (32.4 MHz, $CDCl_3$) δ
6a	30	oil	$C_4H_9OPS_3$ (200.3)	1.40 (t, 3H, CH_3), 2.9- 3.8 (m, 4H, CH_2S), 4.5 (m, 2H, CH_2O)	15.5 (d, J = 5.8, CH_3), 30.3 (d, J = 4.4, CH_2 Et.), 37.1 (CH_2S), 70.5 (d, J = 3.3, CH_2O)	115.0 [c]
6b	40	oil	$C_9H_{11}OPS_3$ (262.2)	3.5 (m, 2H, CH_2S), 4.25 (d, 2H, J = 17.0, CH_2-Ph), 4.50 (m, 2H, CH_2O), 7.3 (m, 5H, $H_{ar.}$)	37.2 (d, J = 0.9, CH_2S), 40.2 (d, J = 4.1, CH_2-Ph), 70.7 (d, J = 3.4, CH_2O), 127.7 (C_4), 128.7 (C_3), 129.0 (C_2), 136.3 (d, J = 6.5 , C_1)	114.0
6c	46	oil	$C_7H_9O_2PS_3$ (252.3)	3.5 (m, 2H, CH_2S), 4.22 (d, 2H, J = 17.0 , CH_2-Fu), 4.5 (m, 2H, CH_2O), 6.3 (m, 2H, $H_{3,4}$ Fu), 7.35 (m, 1H, H_5 Fu)	32.3 (d, J = 3.7, CH_2-Fu), 37.0 (CH_2S), 70.6 (d, J = 3.2, CH_2O), 108.7 (C_3), 110.5 (C_4), 142.4 (C_5), 149.1 (d, J = 5.9, C_2)	77.0
6d	26	oil	$C_5H_{11}OPS_3$ (214.3)	1.38 (t, 3H, CH_3 Et.), 1.53 (d, 3H, CH_3), 2.6-3.9 (m, 4H, CH_2S), 4.7 (m, 1H, CH-O)	15.3 (d, J = 6.3, CH_3 Et.), 19.8 and 20.4 (2 isomers, CH_3), 30.1 (d, J = 4.6, CH_2 Et.), 43.4 (CH_2S), 81.0 and 80.9 (2 isomers, J = 3.9, CH-O)	114.0 [d]
6e	36	98	$C_9H_{11}OPS_3$ (262.7)	1.25 (d, 3H, CH_3), 3.1 (m, 2H, CH_2S), 4.6 (m, 1H, CH-O), 7.55 (m, 5H, $H_{ar.}$)	19.0 and 19.6 (2 isomers, CH_3), 43.7 (CH_2S), 81.0 and 79.0 (2 isomers, J = 4.9, CH-O), 128.9 (d, J = 7.4, C_1), 129.2 (d, J = 2.3, C_3), 130.3 (d, J = 4.1, C_4), 136.6 (d, J = 4.6, C_2)	111.1

TABLE I (*Continued*)

Product	Yield[a] (%)	mp (°C)	Molecular Formula	^{1}H-NMR[b, d] (60 MHz, CDCl$_3$/TMS) δ, ^3J P-H (Hz)	^{13}C-NMR[b, e] (20.1 MHz, CDCl$_3$) δ, J P-C(Hz)	^{31}P-NMR (32.4 MHz, CDCl$_3$) δ
6f	28	69	$C_{10}H_{13}OPS_3$ (276.4)	1.45 (d, 3H, CH$_3$), 3.3 (m, 2H, CH$_2$S), 4.18 (d, 2H, J = 16.0, CH$_2$-Ph), 4.7 (m, 1H, CH-O), 7.3 (m, 5H, H$_{ar.}$)	19.7 and 20.2 (2 isomers, CH$_3$), 39.8 (d, J = 3.9, CH$_2$-Ph), 43.2 (d, J = 0.7, CH$_2$S), 81.1 and 80.9 (2 isomers, J = 3.9, CH-O), 127.6 (C$_4$), 128.6 (C$_3$), 129.0 (C$_2$), 135.8 (d, J = 7.1, C$_1$)	99.7
6g	17	oil	$C_8H_{11}O_2PS_3$ (266.3)	1.47 (d, 3H, CH$_3$), 3.3 (m, 2H, CH$_2$S), 4.21 (d, 2H, J = 16.0, CH$_2$-Ph), 4.6 (m, 1H, CH-O), 6.3 (m, 2H, H$_{3,4}$ Fu), 7.35 (m, 1H, H$_5$ Fu)	19.8 and 20.3 (2 isomers, CH$_3$), 32.2 (d, J = 3.4, CH$_2$-Fu), 43.1 (CH$_2$S), 81.1 and 81.3 (2 isomers, J = 4.1, CH-O), 108.9 (C$_3$), 110.7 (C$_4$), 142.7 (C$_5$), 149.3 (d, J = 6.0, C$_2$)	113.2

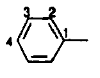
[a] Yield of isolated purified products.

[b] Fu.: furyl group.

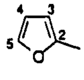
[c] Another minor product is detected but not identified (103.0 ppm, <5%).

[d] Another-minor product is detected but not identified (100.2 ppm, <5%).

[e] Numbering of the atoms in ^{1}H and ^{13}C NMR is the following:



6b,e and f



6c and g

EXPERIMENTAL

Melting points are uncorrected. The ^{1}H-NMR spectra were recorded on a Jeol PMX 60 si. ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker WP 80 (20.1 and 32.4 MHz respectively), using CDCl$_3$ as solvent. Column chromatography was performed on silica gel (Merck Geduran Si 60, 70-230 mesh).

Triethylammonium salts **1**. *General Procedure.* To a well stirred suspension of phosphorus pentasulfide (11.1 g, 5 mmol) in toluene (150 mL), a solution of thiol (20 mmol) and triethylamine (11.1 g, 11 mmol) in toluene (100 mL) is added under a nitrogen atmosphere. The reaction is exothermic and stirring is continued until the temperature decreases. The reaction mixture is then heated under reflux overnight. After cooling to room temperature, the salt is precipitated with petroleum ether or hexane, cooled to − 10°C and filtered. The crude salt is then purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/EtOH (96:4). The purified salt is washed with ether and filtered under vacuum to give **1** in high yields (>90% in most cases).

2-alkyl (or aryl, ...)thio-1,3,2-oxathiaphospholane-2-sulfides **6**. *General Procedure.* A solution of triethylammonium salt **1** (10 mmol) in CHCl$_3$ (50 mL) is cooled to −30°C under a nitrogen atmosphere. The epoxide used (100 mmol) is added in one portion followed a few minutes later by the BF$_3$-Et$_2$O (0,3 g, 2 mmol). The mixture is stirred for 3 to 4 hours at the same temperature and then allowed to warm to room temperature and stirred overnight. The solvent is evaporated and the residue extracted with Et$_2$O (3 × 50 mL). The combined organic solutions are evaporated and the product is separated by column chromatography on silica gel (pentane/ether, 70:30) to give the desired product **6** (Table I).

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