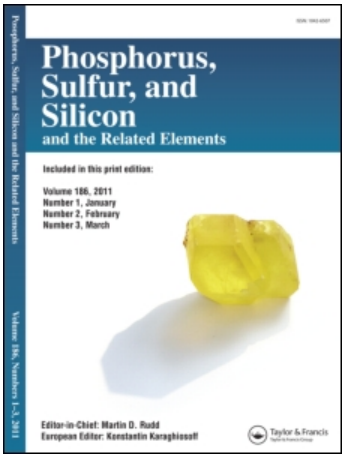

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NEW SYNTHETIC WAY FOR THE PREPARATION OF 1,3,2-OXATHIAPHOSPHOLANE OR 1,3,2-OXATHIAPHOSPHORINANE 2-SULFIDE DERIVATIVES

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1,3,2-oxathia-phospholane or -phosphorinane 2-sulfide derivatives **2** and **3** are readily accessible by reaction of the triethylammonium salts **1** of diesters of the phosphorotetrathioic acid with ω-bromo alcohols under mild conditions.

Key words: Oxathiaphospholane derivatives; oxathiaphosphorinane derivatives; phosphorotetrathioic acid; ω-bromo alcohols.

INTRODUCTION

Although the synthesis of a large number of phosphorus containing heterocycles are well known and extensively described, only a few papers concern the preparation of the titled compounds.

The classical pathway[1] to obtain 1,3,2-oxathia-phospholane or phosphorinane 2-sulfide derivatives consists in the condensation of reagents containing P—Cl bonds such as R—PCl_2 or R—$P(S)Cl_2$ with ω-mercapto alcohols followed for phosphorus (**III**) derivatives by the oxydation of the phosphorus atom with elemental sulfur.[2] This general way can be applied to the synthesis of other heterocycles such as the 1,3,2-dithia- and dioxaphospholane derivatives, using a dithiol or a diol[3] and 1,3,2-thiaza- and oxazaphospholidines from functionalized amines.[4] Due to the use of difunctional reagents in this way, intermolecular reactions may occur during the condensation what could be an explanation for the modest yields generally observed.

We have recently reported[5] the formation of 1,3,2-oxathia-phospholane 2-sulfide derivatives **2** in one step from the triethylammonium phosphorotetrathioates **1** by their regiospecific nucleophilic attack on oxiranes, catalysed by $BF_3 \cdot Et_2O$.

Using the reactivity of salts **1** towards halides,[6] we worked out an easy synthetic method leading to 1,3,2-oxathia-phospholane **2** or phosphorinane 2-sulfide **3** in high yields.

RESULTS AND DISCUSSION

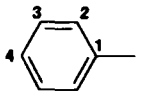
In order to have a better control in the cyclisation process and to be able to generalize the formation of **2**, we tried to synthesize the unsymmetrical triesters **6**

TABLE I

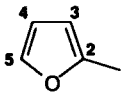
Physical and spectral data of compounds **2a-c** and **3a-c** in $CDCl_3$

Product	Yield (%)	mp (°C)	Molecular Formula	^{1}H-NMR (60 MHz) δ, $^3J_{P-H}$ (Hz)	^{13}C-NMR (20.1 MHz) δ, J_{P-C} (Hz)	^{31}P-NMR (32.4 MHz) δ
2a	73	58	$C_8H_9OPS_3$ (248.3)	2.1-3.7 (m, 2H, CH_2S), 3.7-4.7 (m, 2H, CH_2O), 7.4 (m, 5H, $H_{ar.}$)	37.4 (CH_2S), 71.5 (d, J = 4.6, CH_2O), 128.4 (d, J = 8.6, C1), 129.1 (d, J = 3.4, C3), 130.0 (d, J = 4.2, C4), 135.9 (d, J = 4.7, C2)	113.0
2b	71	31	$C_9H_{11}OPS_3$ (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 (C4), 128.7 (C3), 129.0 (C2), 136.3 (d, J = 6.5 , C1)	113.8
2c	82	oil	$C_7H_8O_2PS_3$ (252.3)	3.5 (m, 2H, CH_2S), 4.22 (d, 2H, J = 17.0 , CH_2S Furf.), 4.5 (m, 2H, CH_2O), 6.3 (m, 2H, $H_{3,4}$ Furf.), 7.35 (m, 1H, H_5 Furf.)	32.3 (d, J = 3.7, CH_2S Furf.), 37.0 (CH_2S), 70.6 (d, J = 3.2, CH_2O), 108.7 (C3), 110.5 (C4), 142.4 (C5), 149.1 (d, J = 5.9, C2)	113.8

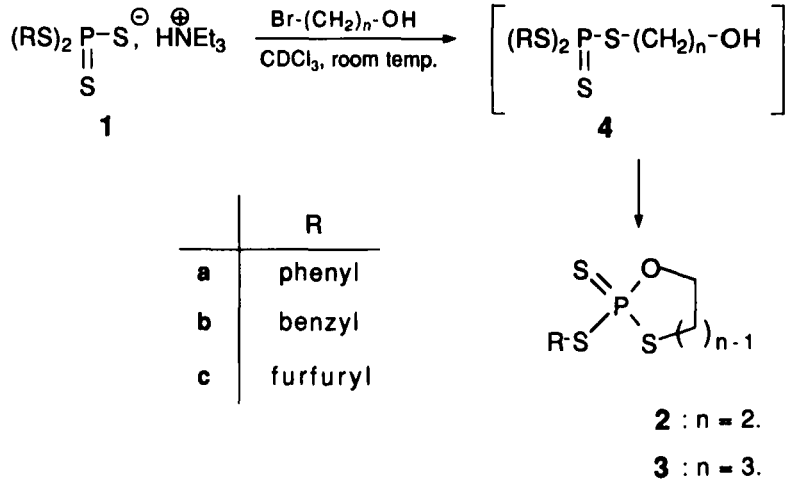
3a	71	87	$C_9H_{11}OPS_3$ (262.2)	1.7-2.4 (m, 2H, CH_2 cycle), 2.7-3.6 (m, 2H, CH_2S), 4.0-4.9 (m, 2H, CH_2O), 7.4 (m, 5H, $H_{ar.}$),	25.8 (d, J = 7.6, CH_2cycle), 30.3 (d, J = 4.3, CH_2S), 70.5 (d, J = 10.6, CH_2O), 127.2 (d, J = 6.9, C_1), 129.3 (d, J = 3.0, C_3), 129.8 (d, J = 3.7, C_4), 135.6 (d, J = 4.8, C_2)	87.2
3b	69	69	$C_{10}H_{13}OPS_3$ (276.4)	1.6 - 2.2 (m, 2H, CH_2cycle), 2.4 - 3.5 (m, 2H, CH_2S), 3.8 - 4.7 (m, 2H, CH_2O), 4.22 (d, 2H, J = 14.0, CH_2-Ph), 7.35 (m, 5H, $H_{ar.}$)	25.5 (d, J = 7.4, CH_2cycle), 30.1 (d, J = 4.0, CH_2S), 37.1 (d, J = 3.3, C_1), 70.3 (d, J = 10.4, CH_2O), 127.4 (C_2) 128.4 (C_4), 128.8 (C_3), 136.1 (d, J = 5.6, C_2)	89.8
3c	77	oil	$C_8H_{11}O_2PS_3$ (266.3)	1.7-2.6 (m, 2H, CH_2 cycle), 2.7-3.7 (m, 2H, CH_2S), 4.0-4.9 (m, 2H, CH_2O), 4.22 (d, 2H, J = 14.0, CH_2S Furf.), 6.3 (m, 2H, $H_{3,4}$ Furf.), 7.35 (m, 1H, H_5 Furf.)	25.5 (d, J = 7.5, CH_2cycle), 29.4 (d, J = 3.0, CH_2S), 30.1 (d, J = 4.4, C_1), 70.2 (d, J = 10.4, CH_2O), 108.9 (C_3), 110.6 (C_4), 142.4 (C_5), 149.2 (d, J = 6.0, C_2)	89.0



for **2a,b** and **3a,b**



for **2c** and **3c**



SCHEME 1

by condensation of salts **1** with 2-bromo ethanol or 3-bromo propanol. Curiously, the expected triesters were not obtained. We have only isolated, after purification by column chromatography, compounds **2** and **3** in high yields (see Table) as well as small amounts of thiols which has been already observed in the formation of **2** with oxiranes, due to the partial decomposition of the salt **1** used (see Scheme 1).

The first step of this reaction presumably leads to the expected unsymmetrical **4** but the terminal alcohol function attacks the phosphorus atom. The ^{1}H NMR spectrum of the crude product shows that the formation of these compounds really does occur during the reaction and not afterwards at the chromatographic stage.

Although the substituents used for this study are quite different in each case, the ^{31}P NMR chemical shifts observed are very close. The nature of the substituent on the phosphorus atom seems not to influence the electron distribution in these heterocycles.

The synthesis of larger rings, using this method, is actually investigated although the possibility of intermolecular reaction probably increases very quickly with the chainlength of the halogenated alcohol.

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_2Cl_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).

1,3,2-oxathiaphospholanes **2** *and 1,3,2-oxathiaphosphorinanes* **3**. *General procedure*. 2-Bromo ethanol (for **2**) or 3-bromo propanol (for **3**) (12 mmol) is added at room temperature to a stirred solution of salt **1** (10 mmol) in $CHCl_3$ (50 mL). The condensation is followed by TLC until all the salt has been consumed. The solvent is evaporated and the residue extracted with Et_2O (3 × 50 mL). The combined organic fractions are evaporated and the product is separated by column chromatography on silica gel (pentane/ether: 70/30) to give the desired product after adequate recristallization in a mixture of pentane and ether.

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