

## Brief Communications

### Reactions of *P*-cyanospirophosphoranes with derivatives of phosphorous acid

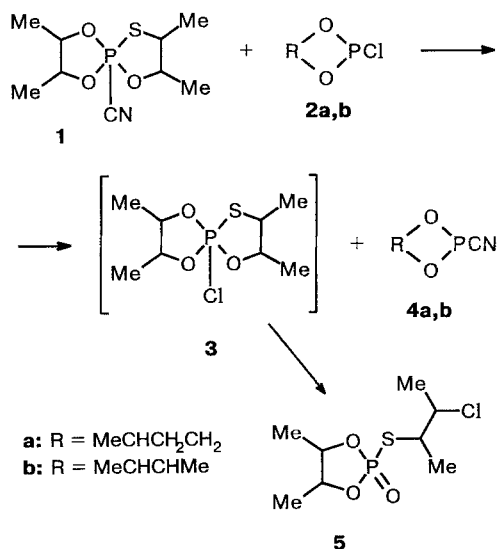
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5-Cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane reacts with some chlorophosphites and amidophosphites to give the corresponding  $P^{III}$ -cyano derivatives.

**Key words:** 5-cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane; chlorophosphites, amidophosphites.

One of the possible approaches to cyano derivatives of  $P^{III}$  is based on the exchange of substituents between



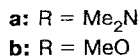
phosphoranes with a P—CN bond and tri-coordinated phosphorus compounds. For this reason, in this work we studied the interaction of 5-cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane (**1**) with various derivatives of phosphorous acid.

When heated in benzene spirophosphorane **1** easily reacts with the corresponding derivative of phosphorous acid **2a,b** replacing the CN group with Cl to form cyanophosphites **4a,b**, respectively, and thiophosphate **5**, the product of rearrangement of the intermediate chlorophosphorane **3**.

In a similar way, the reaction of spirophosphorane **1** with bis(diethylamido)chlorophosphite (**6**) gives rise to diamidocyanophosphite **7** and thiophosphate **5**.



Reaction of hexamethyl triamidophosphite (**8a**) with spirophosphorane **1** in like manner results in the formation of compound **9a** with a *P*-cyano group and the amide of cyclic phosphate **11**.



It is known that spirophosphoranes containing a P—Cl bond can exchange a Cl atom for an ethoxy group of triethyl phosphite.<sup>1</sup> However, compound **1** does not react with triethyl phosphite. Treatment of 2-dimethylamino-4-methyl-1,3,2-dioxaphosphorinane with compound **1** also does not result in exchange of CN for Me<sub>2</sub>N.

**Reaction of 5-cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane (1) with phosphorous acid derivatives (general method).** Equimolar quantities of spirophosphorane and phosphite (**2a,b**, **6**, and **8a,b**) were refluxed in  $C_6H_6$

**Methyl(dimethylamido)cyanophosphite (9b)** could not be separated from benzene. Amidophosphate **11** was isolated: b.p. 79 °C (0.1 Torr),  $d_4^{20}$  1.1479,  $n_D^{20}$  1.4570. Found (%): C, 40.35; H, 7.90.  $C_6H_{14}NO_3P$ . Calculated (%): C, 40.22; H, 7.82.  $^{31}P$  NMR,  $\delta$ : +23.

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