## **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  $P^{\rm III}$ -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<sup>III</sup> 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.

1 + 
$$(Et_2N)_2PCI$$
 —  $(Et_2N)_2PCN$  + 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.

$$1 + (Me_2N)_2PR \longrightarrow PCN + Me_2 + Me_2N + Me_2N$$

We found that if spirophosphorane 1 reacts with methyl bis(dimethylamido)phosphite (8b) the exchange of a Me<sub>2</sub>N group (not a MeO group) for CN takes place, although we could not isolate the corresponding amidocyanophosphite 9b in pure form.

It is known that spirophosphoranes containing a P—Cl bond can exchange a Cl atom for an ethoxy group of triethyl phosphite. 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.

### **Experimental**

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  $C_6H_6$ 

for 20–30 min. The <sup>31</sup>P NMR spectrum of the reaction mixture contained two signals of the expected products corroborating the quantitative yields of cyanophosphites **4a,b**, **7,** and **9a,b**.

The products were isolated by distillation in vacuo.

**2-Cyano-4-methyl-1,3,2-dioxaphosphorinane (4a):** b.p. 35—40 °C (0.08 Torr),  $d_4^{20}$  1.1672,  $n_D^{20}$  1.4660. Found: P, 21.60 %. C<sub>5</sub>H<sub>8</sub>NO<sub>2</sub>P. Calculated: P, 21.38 %. <sup>31</sup>P NMR,  $\delta$ : +105.

**2-Cyano-4,5-dimethyl-1,3,2-dioxaphospholane (4b):** b.p. 35-38 °C (0.1 Torr),  $d_4^{20}$  1.1500,  $n_D^{20}$  1.4570. <sup>31</sup>P NMR,  $\delta$ : +113. Compound **4b** fumes and quickly decomposes in air.

**Bis(diethylamido)cyanophosphite (7):** b.p. 72—74 °C (0.1 Torr),  $d_4^{20}$  0.9667,  $n_D^{20}1.4740$ . <sup>31</sup>P NMR,  $\delta$ : +58 (cf. Ref. 2).

In the syntheses of **4a,b** and 7 thiophosphate **5** was also obtained: b.p. 117-119 °C (0.1 Torr),  $d_4^{20}$  1.2593,  $n_D^{20}$  1.4900–1.4940. <sup>31</sup>P NMR,  $\delta$ : +41 (cf. Ref. 3).

**Bis(dimethylamido)cyanophosphite** (9a): b.p. 40-45 °C (0.2 Torr),  $d_4^{20}$  0.9882,  $n_D^{20}$  1.4730. <sup>31</sup>P NMR,  $\delta$ : +66 (cf. Ref. 4). Isolation of the corresponding amidophosphate 11 in pure form could not be achieved.

**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. <sup>31</sup>P NMR,  $\delta$ : +23.

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