Brief Communications

Reactions of *P*-cyanospirophosphoranes with some thiols and alcohols

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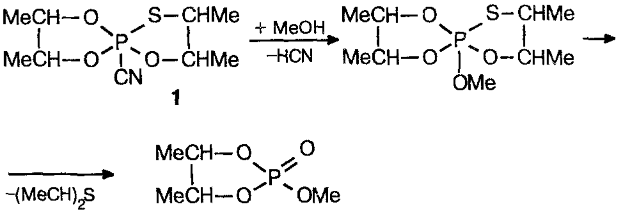
5-Cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane reacts with thiols and secondary alcohols only in the presence of Et_3N.

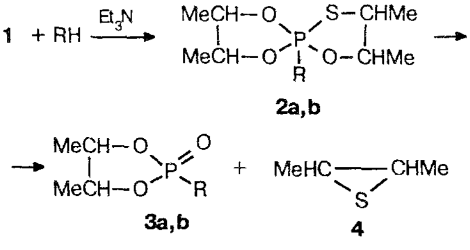
Key words: 5-cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane, 2-propanol, thiols.

It is known that 5-cyano-2,3,7,8-tetramethyl-1,4,6,9-trioxathia-5-phosphaspiro[4.4]nonane (**1**) reacts readily with methanol in CH_2Cl_2 to form a 5-methoxy derivative at the first stage, which decomposes on heating or storage.[1]



The reaction of spirophosphorane **1** with other primary alcohols, *e.g.*, ethanol, proceeds analogously. However, secondary alcohols and thiols do not react with **1** even in boiling benzene.

However, the reactions of **1** with 2-propanol and isobutanethiol in boiling C_6H_6 proceed to completion in the presence of an equimolar amount of triethylamine.



R = Pr^iO (**a**), Bu^iS (**b**)

The reaction with 2-propanol gives a mixture of compounds **2a** (^{31}P NMR, δ −13) and **3a** ($\delta^{31}P$ +12); this transforms completely into **3a** on storage or distillation. Compound **2b** ($\delta^{31}P$ +6) formed from **1** and Bu^iSH is more stable and does not decompose in a CH_2Cl_2 solution in one day. However, it does decompose on distillation to form compound **3b** ($\delta^{31}P$ +40) and 2,3-butylene sulfide (**4**).

It was interesting to investigate the behavior of a bifunctional compound such as 2-mercaptoethanol with respect to **1**; *i.e.*, which of the groups would react: the

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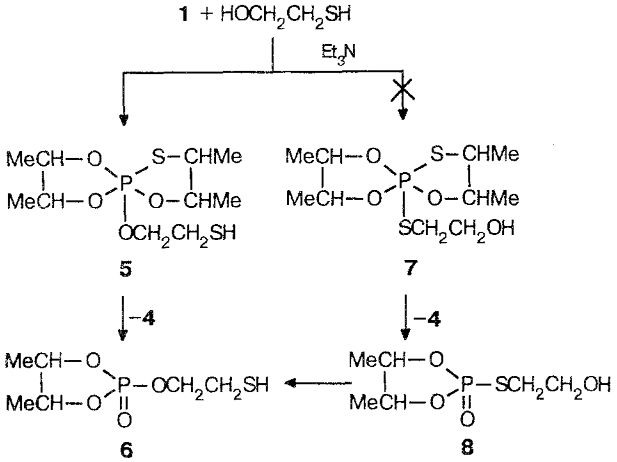
hydroxyl group with the formation of compounds **5** and **6** or the SH group. In the latter case one may expect that in the presence of Et_3N the compound with the P—S bond (**7**) would be obtained, whose consequent transformations would afford products **8** or **6** (the latter, as the result of rearrangement).



It was found that this reaction proceeds with the participation of the hydroxyl group in the presence and in the absence of Et_3N. However, in the presence of Et_3N a mixture of products **5** and **6** is isolated (the former product is predominant), and after one day of storage of the mixture without solvent compound **5** is decomposed, and only the signals of compound **6** are observed in the ^{31}P NMR spectrum. In the absence of Et_3N, a mixture of **6** and 2,3-butylene sulfide is formed practically immediately.

Experimental

Reaction of spirophosphorane 1 with 2-propanol. Et_3N (0.85 g) and Pr^iOH (0.5 g) were added to a solution of compound **1** (2.1 g) in 10 mL of C_6H_6. The mixture was heated for 15 min at 45 °C, and then C_6H_6 and other volatile substances were removed at 0.1 Torr. The ^{31}P NMR spectrum of the residue contains two signals (δ): −13 (**2a**) and +12 (**3a**). After *ca.* 24 h only the signal of **3a** remains. Distillation of the residue gives 1.4 g (85 %) of 2-isopropoxy-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (**3a**), b.p. 78 °C (0.1 Torr), d_4^{20} 1.1286, n_D^{20} 1.4280. Found: P, 15.59 %. $C_7H_{15}O_4P$. Calculated: P, 15.97 %.

Reaction of spirophosphorane 1 with 2-butanethiol. Analogously, from compound **1** (3.9 g) in 20 mL of C_6H_6, Et_3N (1.58 g) and isobutanethiol (1.4 g) product **2b** (4.75 g) was obtained, d_4^{20} 1.1446, n_D^{20} 1.5040. ^{31}P NMR (δ): +6. Distillation of **2b** gives 2.5 g (71 %) of 2-isobutylthio-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (**3b**), b.p. 120 °C (0.1 Torr), d_4^{20} 1.1393, n_D^{20} 1.4780. Found (%): C, 42.93; H, 7.68; P, 14.01. $C_8H_{17}O_3PS$. Calculated (%): C, 42.85; H, 7.59; P, 13.83. ^{31}P NMR (δ): +40. After distillation of **2b** 2,3-butylene sulfide (1 g, 90 %) was isolated from a trap, b.p. 94 °C.

Reaction of spirophosphorane 1 with 2-mercaptoethanol. *A.* A solution of compound **1** (1.34 g) in 5 mL of C_6H_6 was refluxed for 15 min with 2-mercaptoethanol (0.42 g). After removal of C_6H_6 and other volatile substances (including **4**) *in vacuo* (0.2 Torr), heating of the residue at *ca.* 40 °C afforded 2-(2-mercaptoethoxy)-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (**6**) in quantitative yield, d_4^{20} 1.2679, n_D^{20} 1.4750. Found: P, 14.54 %. $C_6H_{13}O_4PS$. Calculated: P, 14.62 %. ^{31}P NMR (δ): +13.

B. A mixture of compounds **5** ($\delta^{31}P$ −11) and **6** ($\delta^{31}P$ +12) in a ratio of 2 : 1 was obtained by heating spirophosphorane **1** (1.4 g), Et_3N (0.56 g), and 2-mercaptoethanol (0.43 g) with reflux in 5 mL of C_6H_6. After storage of the mixture for *ca.* 24 h, only the signal of compound **6** was observed in the ^{31}P NMR spectrun. Phospholane **6** cannot be isolated by distillation due to resinification, probably assisted by an admixture of Et_3N.

References

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