REACTIONS OF 5-CYANO-1,4,6,9-TRIOXATHIA-5-PHOSPHASPIRO[4,4]NONANES WITH COMPOUNDS CONTAINING A LABILE HYDROGEN ATOM

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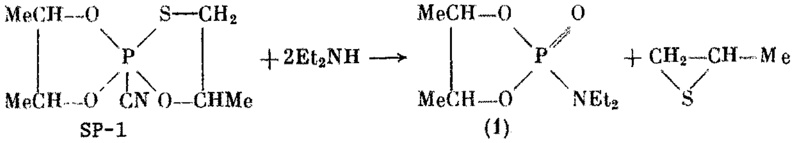
All the investigated reactions of 5-cyano-1,4,6,9-trioxathia-5-phosphaspiro[4,4]nonanes with compounds containing a labile hydrogen atom proceed with the loss of HCN, predominant opening of the oxathiophospholane ring, and formation of 2-oxo-1,3,2-dioxaphospholane derivatives.

Keywords: *5-cyano-1,4,6,9-trioxathia-5-phosphaspiro[4,4]nonanes, 2-oxo-1,3,2-dioxaphospholane derivatives.*

Spirophosphoranes obtained from 2-(2-thiocyanatoalkoxy)-1,3,2-dioxaphospholanes react with an equimolar amount of water to give 2-mercaptoalkyl esters of alkyleneglycolphosphoric acids, which decompose upon distillation to give a phosphorus acid and alkylene sulfide [1].

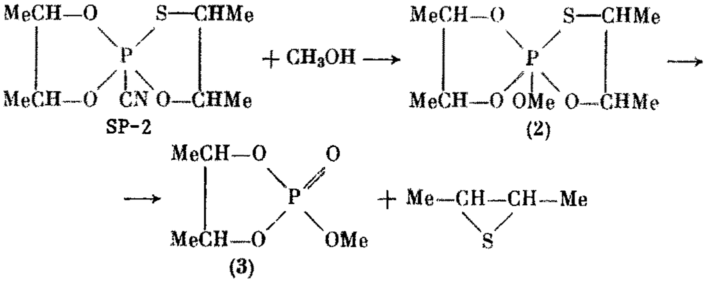
In a continuation of this study, we investigated the reactions of 5-cyano-1,4,6,9-trioxathia-5-phosphaspiro[4,4]nonanes (spirophosphoranes, SP) with compounds containing a labile hydrogen atom, including diethylamine, methanol, hydrogen chloride with thiocyanic acid, and acetic acid.

The reaction of SP with two equivalents of diethylamine give the diethylamide of alkyleneglycolphosphoric acid and an alkylene sulfide.



A mixture of SP-1 and **1** are obtained if only one equivalent of diethylamine is taken in this reaction.

The reaction of SP under mild conditions with methanol leads initially to 5-methoxy derivatives, which decompose upon distillation or brief storage at ~20°C to give the methyl ester of alkyleneglycolphosphoric acid and alkylene sulfide.



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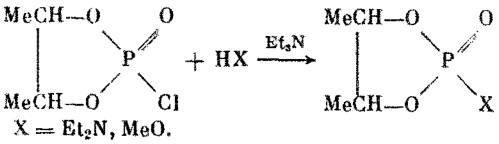
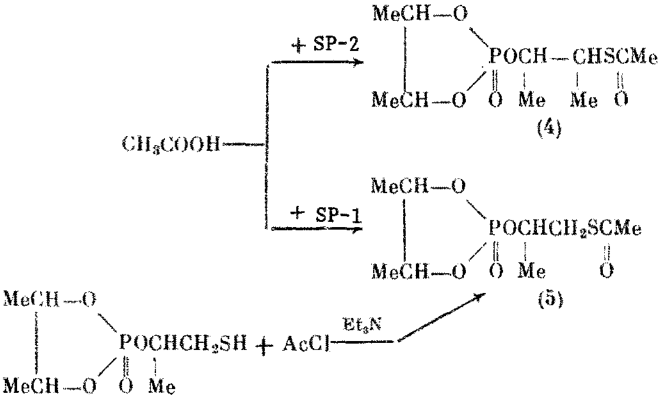
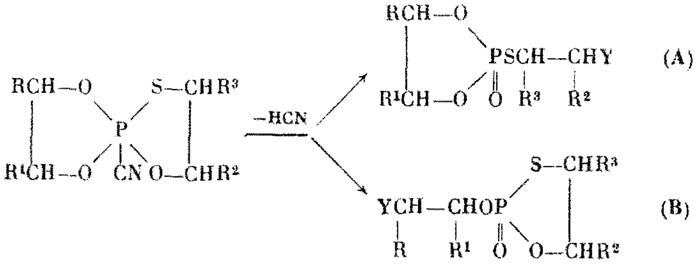
The physical indices and IR spectra of **1** and **3** are identical to those of samples obtained according to the following scheme:



The reaction of SP with acetic acid was carried out in benzene or CH_2Cl_2 and gave the following thioacetates, one of which was obtained previously from the mercaptoalkyl ester and acetyl chloride [2].



The reaction of spirophosphoranes with hydrogen chloride and thiocyanic acid in ether gives compounds with ^{31}P NMR chemical shifts of 40 and 42 ppm, which may correspond to structures **A** and **B**.



The formation of butylene sulfide is not observed in the hydrolysis of the product of the reaction of SP-2 with HCl. Thus, the products of the reaction of SP with HCl and HCN presumably have structure **A**, although opening of the dioxaphospholane ring depending on substituents R, R^1, R^2, and R^3 is not excluded.

Structure **A**. $R = R^1 = R^2 = R^3 = Me$; $Y = Cl$ (**6**).

$R = R^1 = R^2 = Me$; $R^3 = H$; $Y = SCN$ (**7**).

Thus, all the reactions studied for spirophosphoranes proceed with the loss of HCN, opening and, sometimes, decomposition of the oxathiaphospholane ring, and formation of derivatives of 2-oxo-1,3,2-dioxaphospholanes.

EXPERIMENTAL

Reaction of Spirophosphoranes with Diethylamine. A sample of 1.92 g (1:2) diethylamine in 10 ml benzene was added to 3.1 g SP-1 in 10 ml benzene. Warming was not noted. The mixture was heated at reflux for 15 min. The volatile components were evaporated in vacuum at 10 mm Hg and the residue was distilled to give 1.9 g (69%) 1-oxo-2-diethylamino-4,5-dimethyl-1,3,2-dioxaphospholane (**1**), bp 73-78°C (0.08 mm Hg), d_4^{20} 1.1136, n_D^{20} 1.4555. Found, %: P 14.45. $C_8H_{18}NO_3P$. Calculated, %: P 14.97. δ_P 21 ppm.

Reaction of Spirophosphoranes with Methanol. A mixture of 6.5 g SP-2 was dissolved in 40 ml CH_2Cl_2 and 0.835 g methanol was added. The mixture was heated at reflux for 15 min. The solvent and the volatile compounds were evaporated at 10 and, then, 0.1 mm Hg without heating. The following constants were determined immediately for **2**: d_4^{20} 1.1813, n_D^{20} 1.4850, δ_P from −6 to −8 ppm. Upon storage at ~20°C, **2** decomposes into butenyl sulfide with bp 92-94°C (760 mm Hg) and 2-oxo-2-methoxy-4,5-dimethyl-1,3,2-dioxaphospholane, bp 70-72°C (0.1 mm Hg), d_4^{20} 1.2111, n_D^{20} 1.4330. Found, %: C 36.40; H 6.54. $C_5H_{11}O_4P$. Calculated, %: C 36.14; H 6.62. δ_P 13 ppm.

Reaction of Spirophosphoranes with Acetic Acid. A sample of 5.8 g SP-2 was dissolved in 10 ml benzene and 1.39 g acetic acid in 10 ml benzene was added. Slight warming was noted. The mixture was heated at reflux for 10 min. The volatile compounds were distilled off at 0.1 mm Hg. The residue had the following physical constants: d_4^{20} 1.2025, n_D^{20} 1.4750, δ_P 40, 12 ppm. The constants were virtually unchanged on distillation of **4**: bp 126°C (0.06 mm Hg), d_4^{20} 1.2068, n_D^{20} 1.4771. Found, %: C 42.38; H 6.69; P 11.15. $C_{10}H_{19}O_5PS$. Calculated, %: C 42.55; H 6.73; P 10.99. δ_P 12 ppm.

The reaction of equimolar amounts of SP-1 and acetic acid in CH_2Cl_2 gave thioacetate **5**: d_4^{20} 1.2265, n_D^{20} 1.4740. δ_P 12 ppm (d_4^{20} 1.2288, n_D^{20} 1.4740. δ_P 12 ppm [2]).

Reaction of Spirophosphoranes with Hydrochloric and Thiocyanic Acids. Equimolar amounts of SP and acid were dissolved in ether and heated at reflux for 10-15 min. The volatile components were evaporated at 10 mm Hg and the residue was distilled.

6: bp 115-118°C (0.15 mm Hg), d_4^{20} 1.2561, n_D^{20} 1.4915. Found, %: P 11.59. $C_8H_{16}ClO_3PS$. Calculated, %: P 11.99. δ_P 40 ppm. The yield was 58%.

7: bp 97-102°C (0.06 mm Hg), d_4^{20} 1.2808, n_D^{20} 1.5198. Found, %: C 35.90; H 5.18; P 11.53. $C_8H_{14}NO_3PS_2$. Calculated, %: C 35.95; H 5.24; P 11.61. δ_P 41 ppm. The yield was 53%.

REFERENCES

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