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Abstract

Full Text

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Interaction of Phosphorus Pentasulfide with Alcohols in the Presence of Bases

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Chemistry

The interaction of phosphorus pentasulfide with alcohols and phenols has long been used for the synthesis of esters of dithiophosphoric acid (^1). The correct overall reaction equation

$$4ROH + P_2S_5 \rightarrow 2(RO)_2P(S)SH + H_2S$$

was established by Pishchimuka (^2). Later the structure of the resulting acids was proved (^3). Diesters of dithiophosphoric acid in pure form were obtained by Kabachnik and Mastryukova (^4). From the reaction products many authors also isolated neutral esters of dithiophosphoric acid and esters of polythiopolyphosphoric acids (^2, ^5).

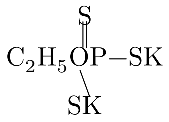
In our works (^6) we investigated the interaction of phosphorus pentasulfide with β-substituted ethanols in order to determine the influence of substituents on the course of the reaction. The products isolated and studied after carrying out the interaction of phosphorus pentasulfide and β-dialkylaminoethanols gave grounds to suppose that in this reaction phosphorus pentasulfide reacts according to an equation analogous to that of phosphorus pentoxide in reactions with alcohols (^7).

To test this supposition, we investigated the interaction of phosphorus pentasulfide with a mixture of alcohol and triethylamine in the molar ratio 1 : 3 : 3 (^8).

$$P_2S_5 + 3ROH + 3(C_2H_5)_3N \rightarrow (RO)_2P(S)SH \cdot (C_2H_5)_3N +$$

$$+ROP(S)(SH)_2 \cdot 2(C_2H_5)_3N.$$

The mixture of triethylamine salts obtained as a result of the reaction was converted into potassium salts and separated. The yield was 70–80%. Potassium O,O-diethyl dithiophosphate isolated in this way has m.p. 195° in a pure and mixed sample with an authentic specimen (⁀9). Potassium O-ethyl trithiophosphate (1) consists of colorless crystals, gradually decomposing at $T > 200°$, insoluble in acetone, alcohol, and other organic solvents, and readily soluble in water. Its aqueous solutions are unstable and decompose with evolution of hydrogen sulfide. The structure of potassium O-ethyl trithiophosphate



$$C_2H_5O\underset{SK}{\overset{S}{\overset{\|}{P}}}-SK \qquad (1)$$

is proved by alkylation with ethyl bromide. The ester obtained has b.p. 155–156° at 20 mm, n_D^{20} 1.5578, d_4^{20} 1.1577, MR_D found 64.16, calculated 64.92, which corresponds to the literature data (⁀2). The complex compound prepared from the ester and mercuric iodide, according to Pishchimuka (⁀2), melts in a pure and mixed sample with an authentic specimen at 112–113°.

Methyl, propyl, *n*-butyl, and cyclohexyl alcohols, phenol, and *p*-nitrophenol interact with phosphorus pentasulfide in an entirely similar manner. Regardless of whether a mixture of the alcohol with triethylamine is used, or a solution of caustic potash in the alcohol, or a solution of potassium alcoholate in the corresponding alcohol, as a result of the rapid reaction the lower aliphatic alcohols give the two products indicated above in practically quantitative yield in a ratio of 1 : 1.

Thus it has been established that phosphorus pentasulfide, in the presence of a base, reacts with hydroxyl derivatives analogously to phosphorus pentoxide. The role of the base apparently consists in stabilizing the monoester of trithiophosphoric acid, which, under the usual conditions for carrying out the reaction between phosphorus pentasulfide and alcohols, evidently reacts with a fourth molecule of the hydroxyl derivative according to the scheme:

$$P_2S_5 + 3ROH \rightarrow (RO)_2P(S)SH + ROP(S)(SH)_2,$$

$$ROP(S)(SH)_2 + ROH \rightarrow (RO)_2P(S)SH + H_2S.$$

We are currently continuing the study of the interaction described with other alcohols and phosphorus sulfides, as well as the properties of salts of monoesters of trithiophosphoric acid.

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