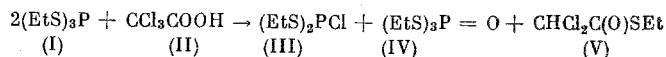


# UNUSUAL REACTION OF TRIALKYL TRITHIOPHOSPHITES WITH TRICHLOROACETIC ACID

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We found that the reaction of triethyl trithiophosphite (I) with trichloroacetic acid (II) takes place with the formation of bis(ethylthio)phosphorous chloride (III), triethyl trithiophosphate (IV), and S-ethyl dichlorothioacetic acid (V), rather than according to the acidolysis reaction scheme of S-esters of thiophosphorous acid in [1]:



The structures of the products obtained were confirmed by the IR and NMR spectra, as well as by comparison of the physicochemical constants with the literature data. Tripropyl trithiophosphite reacts similarly with trichloroacetic acid.

A 12.55-g portion (0.06 mole) of trithiophosphite I was given an addition of 4.8 g (0.03 mole) of trichloroacetic acid. The reaction mixture was held at ~20°C for 30 h and fractionated. Distillation yielded: 4.4 g (79%) of acid chloride III with bp 109–110°C (10 mm Hg),  $n_D^{20}$  1.5812, and  $\delta_P$  188 ppm (compare [2]), 5.6 g (83%) of trithiophosphate IV with bp 94–95°C (0.08 mm Hg),  $n_D^{20}$  1.5731, and  $\delta_P$  61 ppm, which correspond to the data in [3], and 2.2 g (51%) of S-ethyl dichlorothioacetic acid with bp 78–80°C (10 mm Hg) and  $n_D^{20}$  1.5189. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 620 (C–S), 757, 797 (C–Cl), 1695 (C=O). PMR spectrum ( $\delta$ , ppm): 1.31 (t,  $\text{H}_3\text{C}$ ,  $^3J_{\text{HH}} = 7$  Hz), 3.01 (q,  $\text{H}_2\text{C}$ ), 6.12 (s, HC). Found: C, 27.31; H, 3.42; Cl, 41.28; S, 18.01%. Calculated for  $\text{C}_4\text{H}_6\text{Cl}_2\text{OS}$ : C, 27.75; H, 3.46; Cl, 41.04; S, 18.49%.

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