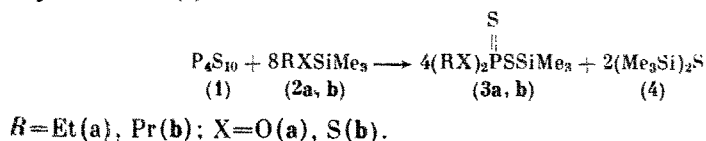


S-TRIMETHYLSILYL DITHIO- AND TETRATHIOPHOSPHATES

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S-Trimethylsilyl dithiophosphates are obtained by the reaction of phosphorus dithio acids or their ammonium salts with silylating agents: 1,1,1,3,3,3-hexamethyldisilazane [1], trimethylsilyl isocyanate, its thio analog, cyclohexenoltrimethylsilane [2], or trimethylchlorosilane [3]. Trimethylsilyl tetrathiophosphates have not been described. We have proposed a new method for the preparation of S-silyl esters of dithio- and tetrathiophosphoric acids by the reaction of tetraphosphorus decasulfide with alcohols and thiols, whose hydroxyl and sulfhydryl groups are protected by a trimethylsilyl group. Thus, we have found that tetraphosphorus decasulfide (1) reacts with ethoxytrimethylsilane (2a) and propylthiotrimethylsilane (2b) at 40°C for 10 h (2a) or 20°C for 3 h (2b) to give O,O-diethyl S-trimethylsilyl dithiophosphate (3a) and dipropyl(trimethylsilyl) tetrathiophosphate (3b), respectively, and hexamethyldisilthiane (4).



Products (3a) and (3b) were separated from the reaction mixture by molecular distillation at 90-115°C (0.02 mm). Product (3a) was further purified by distillation in vacuum.

O,O-Diethyl S-trimethylsilyl dithiophosphate (3a) was obtained in 81% yield, bp 59-60°C (0.02 mm), n_D^{20} 1.5141 [3].

Dipropyl(trimethylsilyl) tetrathiophosphate (3b) was obtained in 95% yield. The temperature of the molecular distillation apparatus was 110-115°C (0.02 mm), d_4^{20} 1.0628, n_D^{20} 1.5650. IR spectrum (ν , cm^{-1}): 1255 s (δ_s [$\text{CH}_3(\text{Si})$]), 855 v.s (ρ [$\text{CH}_3(\text{Si})$]), 668 v.s [$\nu(\text{P}=\text{S})$], 548 sh, 523 v.s ($\nu(\text{PS, PCS, PSSi})$). PMR spectrum at 60 MHz in CCl_4 with benzene as the internal standard (δ , ppm, J , Hz): 0.80 s (9H, CH_3Si), 1.27 t (6H, CH_3C , $^3J_{\text{HH}} = 6.5$), 1.70-2.25 m (4H, CH_2CC , $^3J_{\text{HH}} = 6.5$), 3.07 d.q (4H, CH_2SP , $^3J_{\text{HH}} = 6.5$, $^3J_{\text{PH}} = 16.0$). ^{31}P NMR spectrum at 10.2 MHz (from 85% H_3PO_4): δP 83 ppm. Mass spectrum at 70 eV, m/z : 319 [$\text{M} + \text{H}$] $^+$. Found, %: C 33.38; H 7.64; P 9.60; S 40.03; Si 8.66. $\text{C}_9\text{H}_{23}\text{PS}_4\text{Si}$. Calculated, %: C 33.96; H 7.30; P 9.74; S 40.21; Si 8.80.

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