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**).

$$\underset{(1)}{P_4S_{10}} + 8\underset{(2a,\,b)}{RXSiMe_3} \longrightarrow 4\underset{(3a,\,b)}{(RX)_2P(S)SiMe_3} + 2\underset{(4)}{(Me_3Si)_2S}$$

R=Et(a), Pr(b); X=O(a), S(b).

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 [CH_3(Si)]), 855 v.s (ρ[CH_3(Si)]), 668 v.s [ν(P=S)], 548 sh, 523 v.s (ν(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, $^3J_{HH}$ = 6.5), 1.70-2.25 m (4H, CH_2CC, $^3J_{HH}$ = 6.5), 3.07 d.q (4H, CH_2SP, $^3J_{HH}$ = 6.5, $^3J_{PH}$ = 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 $[M + H]^+$. Found, %: C 33.38; H 7.64; P 9.60; S 40.03; Si 8.66. $C_9H_{23}PS_4Si$. Calculated, %: C 33.96; H 7.30; P 9.74; S 40.21; Si 8.80.

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