

SHORT
COMMUNICATIONS

Synthesis and Thermal Stability of S-Trimethylsilyl-S'-ethyl(diethylamido)trithiophosphate

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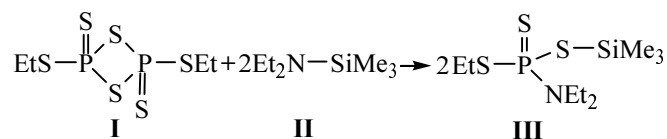
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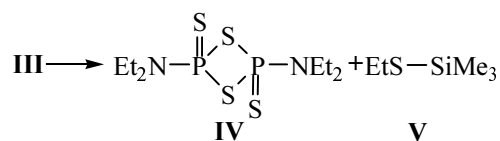
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S-Trimethylsilylbis(dialkylamido)dithiophosphates obtained by reaction of tetraphosphorus decasulfide with trimethyl(dialkylamino)silanes [1] show low heat resistance and at long storage at ~20°C or at a vacuum distillation are converted into bis(tetraalkyldiamidothiophosphoryl) sulfides and bis(trimethylsilyl) sulfide. The thermal stability and chemical behavior of S-trimethylsilyl esters of amidotrithiophosphoric acids containing mixed dialkylamino and alkylthio groups at the phosphorus atom with a fragment NP(S)(SR)S–Si were not previously investigated. We synthesized these compounds by reaction of Davy reagent alkyl homologs with aminosilanes. It was found that the reaction of 2,4-bis-(ethylthio)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**I**) with trimethyl(diethylamino)silane (**II**) at 70°C within 1 h afforded S-trimethylsilyl-S'-ethyl-(diethylamido)-trithiophosphate (**III**).



It was established by differential thermal analysis that the start of the thermal transformations of compound **III** occurred at 99°C. At the storage of compound **III** in a sealed ampule at ~20°C for ~6 months we observed



a partial formation of 2,4-bis-(diethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**IV**) and trimethyl-(ethylthio)silane (**V**).

Physical constants and IR, ¹H and ³¹P NMR and mass spectra of compound **IV** are in agreement with the data from [2]. The molecular and crystal structure of compound **IV** was established by X-ray diffraction analysis. Compound **IV** crystallized in the *trans*-configuration.

S-Trimethylsilyl-S'-ethyl(diethylamido)trithiophosphate (III). To 20.8 g (143.3 mmol) of aminosilane **II** was added by portions at stirring in a flow of dry argon at 40°C 22.2 g (71.6 mmol) of phosphetane **I**. The mixture was stirred for 9 h at 50°C and then filtered. The volatile compounds were removed in a vacuum within 2 h at 0.1 and 0.02 mm Hg at heating to 40–50°C. The residue was subjected to molecular film distillation at heating to 100°C and 0.02 mm Hg. We isolated 21.3 g (49%) of compound **III**, n_D^{20} 1.5021, d_4^{20} 1.0639. IR spectrum (from liquid film), cm^{-1} : 2980, 2935, 2880, 2815 [$\text{CH}_3(\text{Si})$ s], (CH_3 as, s; CH_2 as, s), 1455 (CH_3 as), 1385 (CH_3 as), 1260 [$\text{CH}_3(\text{Si})$ s], 1025 (C–N–C as), 855 [$\text{CH}_3(\text{Si})$], 665 (P=S), 560, 555, 515 (P–SC, S–Si). ¹H NMR spectrum (CCl_4), δ , ppm: 0.53 s [9H, (CH_3)₃Si], 1.17 t [6H, (CH_3CH_2)₂NP, J 7.0 Hz], 1.40 t (3H, $\text{CH}_3\text{CH}_2\text{S}$, J 7.5 Hz), 2.95 d.q (2H, $\text{CH}_3\text{CH}_2\text{SP}$, J 7.5 and 15.0 Hz), 3.36 d.q [4H, (CH_3CH_2)₂NP, J 7.0 and 14.0 Hz]. ³¹P NMR spectrum (CCl_4), δ , ppm: 83.3. Mass spectrum (electron impact), m/z (I_{rel} , %): 301 [M]⁺ (10). Found, %: P 10.59; S 32.10; Si 9.44.

C₉H₂₄NPS₃Si. Calculated, %: P 10.29; S 31.85; Si 9.29. *M* 301.1.

2,4-Bis-(diethylamido)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (IV). In a sealed ampule 7.0 g (23.2 mmol) of compound **III** was kept at ~20°C for 6 months. The precipitate formed was filtered off, washed with CH₂Cl₂, and dried for 2 h in a vacuum (0.02 mm Hg) at 40°C collecting the volatile fraction into a trap cooled with liquid nitrogen. Yield 1.2 g (31%), mp 143°C (publ.: mp 143–145°C [2]). Found, %: C 28.35; H 6.22; N 7.94; P 18.06; S 38.33. C₈H₂₀N₂P₂S₄. Calculated, %: C 28.74; H 6.05; N 8.38; P 18.54; S 38.29.

By distillation of the volatile fraction we obtained 1.0 g (32%) of ethylthiosilane **V**, bp 128–130°C, *n*_D²⁰ 1.4509 (publ.: bp 130°C, *n*_D²⁰ 1.4512 [3]).

IR spectra were recorded on a spectrophotometer UR-20. ¹H NMR spectra (400 MHz) were registered on a spectrometer Bruker MSL-400 (lock CDCl₃), internal reference (Me₃Si)₂O, ³¹P NMR spectra were obtained on a spectrometer Bruker CXP-100 (36.5 MHz), external reference 85% H₃PO₄. Thermal effects were established using thermobalance purchased from Setaram in the mode of differential thermal analysis employing a custom-made heating oven. X-ray diffraction analysis was carried out on an automatic four-circle diffractometer

Enraf-Nonius CAD-4 (λMoK_α 0.71073 Å). Crystals of compound **IV** monoclinic, unit cell parameters at –150°C: *a* 7.940(2), *b* 12.435(4), *c* 7.970(3) Å, β 100.40(2)°, *V* 774.0(4) Å³, *Z* 2, *d*_{calc} 1.68 g/cm³, space group P2₁/*n* (the molecule in a special position in the symmetry center, the complete X-ray diffraction data will be published later). The structure was solved applying the program SIR [4] and the program package MoLEN [5].

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