O,S-BIS(TRIMETHYLSILYL)-4-ALKOXYPHENYLDITHIOPHOSPHONATES

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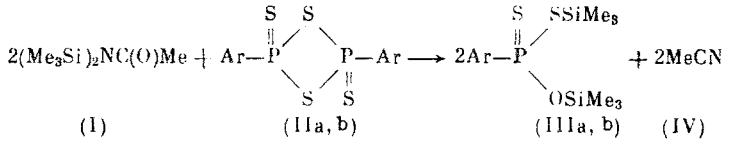
We have found that N,N-bis(trimethylsilyl)acetamide (I) reacts with 2,4-bis(4-alkoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes (IIa) and (IIb) to give O,S-bis(trimethylsilyl)-4-alkoxyphenyldithiophosphonates (IIIa) and (IIIb) as well as acetonitrile (IV). The reaction with (IIa) was carried out at 20°C over seven days, while the reaction with (IIb) was carried out at 50°C over 2.5 h.



(I) (IIa, b) (IIIa, b) (IV)

Ar = 4-$MeOC_6H_4$ (a), 4-$EtOC_6H_4$ (b).

IR spectra of (IIIa) and (IIIb) (ν, cm^{-1}): 3075 w (:C–H, arom), 1598 m (C···C, arom), 1258 s {$\delta_s[CH_3(Si)]$}, 1030 v.s.br (P–O–Si_{as}), 770 m (P–O–Si_s), 630 m (P=S). ^{31}P NMR spectra at 162 MHz relative to 85% H_3PO_4: (IIIa), 75.2 ppm; (IIIb), 75.3 ppm.

O,S-Bis(trimethylsilyl)-4-methoxyphenyldithiophosphonate (IIIa) was obtained in 68.2% yield, injector thermocouple temperature 125-130°C (0.02 mm), d_4^{20} 1.1129, n_D^{20} 1.5564. PMR spectrum at 60 MHz in CCl_4 (δ, ppm, J, Hz): 0.37 s (9H, CH_3SiO), 0.43 s (9H, CH_3SiS), 3.85 s (3H, CH_3O), 6.87 d.d (2H, 3-$H_2C_6H_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 4.0), 7.87 d.d (2H, 2-$H_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 15.0). Found, %: C 42.67; H 6.77; P 8.43; S 17.59; Si 15.28; mass spectrum (100 eV), m/z $[M + H]^+$ 365. $C_{13}H_{25}O_2PS_2Si_2$. Calculated, %: C 42.84; H 6.93; P 8.51; S 17.56; Si 15.37; [M + H] 365.

O,S-Bis(trimethylsilyl)-4-ethoxyphenyldithiophosphonate (IIIb) was obtained in 80.8% yield, injector thermocouple temperature 130-140°C (0.02 mm), d_4^{20} 1.0726, n_D^{20} 1.5465. PMR spectrum at 60 MHz in CCl_4 (δ, ppm, J, Hz): 0.35 s (9H, CH_3SiO), 0.37 s (9H, CH_3SiS), 1.45 t (3H, CH_3CO, $^3J_{HH}$ 7.0), 4.07 q (2H, CH_2O, $^3J_{HH}$ 7.0), 6.87 d.d (2H, 3-$H_2C_6H_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 4.0), 7.86 d.d (2H, 2-$H_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 14.5). Found, %: C 44.23; H 7.27; P 7.82; S 17.14; Si 13.81. $C_{14}H_{27}O_2PS_2Si_2$. Calculated, %: C 44.43; H 7.21; P 8.19; S 16.91; Si 14.80.

Acetonitrile (IV) was also obtained in 90.9-95.0% yield, bp 82-83°C, n_D^{20} 1.3447 [1].

LITERATURE CITED

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