S,S'-DIALKYLTRIMETHYLSILYLDITHIOPHOSPHITES

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Silylphosphites containing RS groups at the phosphorus atom have not been reported. We have found that S,S'-dialkyldithiochlorophosphites upon heating and the elimination of trimethylchlorosilane and acetonitrile react with bis(trimethylsilyl)acetamide to form new silylphosphite derivatives, S,S'-dialkyltrimethylsilyldithiophosphites (I) and (II)

$$(RS)_2PCl + (Me_3Si)_2NC(O)Me \xrightarrow[-Me_3SiCl,-MeCN]{} \underset{(I),(II)}{(RS)_2POSiMe_3}$$

R = Et (I) and n-Bu (II).

The IR spectra of (I) and (II) (ν, cm^{-1}): 1255, 855 (CH_3Si), 958-956 (P—O—Si), 650 (C—S), 580-480 (P—S). ^{31}P NMR spectra at 10.2 MHz relative to 85% H_3PO_4: (I) 168, (II) 163 ppm.

The mild hydrolysis of silylphosphites (I) and (II) leads to unstable S,S'dialkyldithiophosphites with δP 28 ppm, J_{PH} = 632 Hz, which are difficult to prepare by other methods [1, 2].

S,S'-Diethyltrimethylsilyldithiophosphite (I) was obtained in 53.6% yield, bp 118-120°C (10 mm), d_4^{20} 0.9891, n_D^{20} 1.4936. PMR spectrum at 60 MHz in benzene (δ, ppm, J, Hz): 0.32 s (CH_3Si), 1.32 t (CH_3CS), $^3J_{HH}$ = 7.5), 2.77 d. q (CH_2S, $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 9.0). Found, %: C 35.01, H 7.86, P 13.09, S 25.95, Si 11.72. $C_{17}H_{19}OPS_2Si$. Calculated, %: C 34.71, H 7.85, P 12.81, S 26.44, Si 11.57.

S,S'-Dibutyltrimethylsilyldithiophosphite (II) was obtained in 55.5% yield, bp 94°C (0.03 mm), d_4^{20} 0.9794, n_D^{20} 1.4970. PMR spectrum in CCl_4 (δ, ppm, J, Hz): 0.25 s (CH_3Si), 0.74-1.10 m (CH_3C), 1.25-1.82 m (CH_2CH_2C), 2.73 d. t (CH_2S, $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 9.0). Found, %: C 44.59, H 9.10, P 10.71, S 21.77, Si 9.66. $C_{11}H_{27}OPS_2Si$. Calculated, %: C 44.30, H 9.06, P 10.40, S 21.48, Si 9.40.

LITERATURE CITED

1. S. F. Sorokina, A. I. Zavalishina and É. E. Nifant'ev, Zh. Obshch. Khim., 43, 750 (1973).
2. É. E. Nifant'ev, A. I. Zavalishina, S. F. Sorokina, and A. A. Borisenko, Zh. Obshch. Khim., 46, 471 (1976).

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