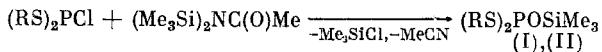


S,S'-DIALKYLTRIMETHYLSILYL DITHIOPHOSPHITES

V. A. Al'fonsov, M. A. Pudovik,
I. S. Nizamov, A. G. Trusenev,
E. S. Batyeva, and A. N. Pudovik

UDC 542.91:547.1'128'118

Silylphosphites containing RS groups at the phosphorus atom have not been reported. We have found that S,S'-dialkyldithioclorophosphites 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)



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'-dialkyl-dithiophosphites with δ_{P} 28 ppm, $J_{\text{PH}} = 632$ 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), $^3J_{\text{HH}} = 7.5$, 2.77 d. q (CH_2S , $^3J_{\text{HH}} = 7.5$, $^3J_{\text{HP}} = 9.0$). Found, %: C 35.01, H 7.86, P 13.09, S 25.95, Si 11.72. $\text{C}_{17}\text{H}_{19}\text{OPS}_2\text{Si}$. 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 ($\text{CH}_2\text{CH}_2\text{C}$), 2.73 d. t (CH_2S , $^3J_{\text{HH}} = 7.5$, $^3J_{\text{HP}} = 9.0$). Found, %: C 44.59, H 9.10, P 10.71, S 21.77, Si 9.66. $\text{C}_{11}\text{H}_{22}\text{OPS}_2\text{Si}$. 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).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, p. 2868, December, 1987. Original article submitted July 1, 1987.