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> SHORT COMMUNICATIONS

Reaction of *O*,*O*-Diethyl -*S*-Trimethylsilyl Dithiophosphate with Diethyl 3-Methyl-1,2-butadienylphosphonate

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It was found previously that S-trimethylsilyl esters derived from phosphorus dithio acids readily add at double carbon-heteroelement bonds of various unsaturated systems [1–4], including such heterocumulenes as isocyanates, sulfenylamines, and carbodiimides [4, 5]. We have studied the reaction of O,O-diethyl S-trimethylsilyl dithiophosphate with diethyl 3-methyl-1.2-butadienylphosphonate, i.e., with a compound having purely carbon-based heterocumulene system. Mixing of 2.58 g (0.01 mol) of O,O-diethyl S-trimethylsilyl dithiophosphate with 2.04 g (0.01 mol) of diethyl 3-methyl-1,2-butadienylphosphonate was accompanied by vigorous heat evolution, and the mixture warmed up to 110°C. It was kept for 3 h at 90°C under argon, and the characteristic absorption band due to stretching vibrations of the allene system (1963 cm^{-1}) was conserved in the IR spectrum. In the ¹H NMR spectrum of the reaction mixture, a multiplet typical of an SCH₂ group appeared at δ 2.98 ppm (PSCH₂CH₃). By vacuum distillation we isolated O,O,S-triethyl dithiophosphate (I) whose physical constants coincided with those reported in [6]. Ethyl trimethylsilyl 3-methyl-1,2-butadienylphosphonate (II) formed as a result of dealkylation of the ethoxy fragment in the initial diethyl phosphonate with S-trimethylsilyl dithiophosphate readily undergoes hydrolysis on storage.

 $EtO = CH = C = CMe_2 + (EtO)_2P(S)SSiMe_3$ $EtO = CH = C = CMe_2 + (EtO)_2P(S)SEt$ $Me_3SiO = I = II$

The high dealkylating activity of *S*-silyl dithiophosphates, which originates from the low energy of dissociation of the S–Si bond in combination with fairly high mobility of the trimethylsilyl group and considerable affinity of silicon to oxygen, was also observed previously in their reactions with keto phosphonates and phosphites [7].

0,0,S-Triethyl dithiophosphate (I). Yield 1.48 g (69%), bp 52–54°C (0.8 mm), $n_D^{20} = 1.4998$; published data [6]: bp 113°C (9 mm), $n_D^{20} = 1.5020$. IR spectrum (film), v, cm⁻¹ : 480 (P–S); 660 (P=S); 964, 1024 (P–O–C); 1128–1192 (P–O–C). ³¹P NMR spectrum (CDCl₃): δ_P 92 ppm.

Ethyl trimethylsilyl 3-methyl-1,2-butadienylphosphonate (II). Yield 1.54 g (62%), bp 87– 92°C (0.8 mm), $n_D^{20} = 1.4602$. IR spectrum (film), v, cm⁻¹: 848 [Si(CH₃)₃]; 968–1032 (P–O–C); 1128, 1164 (P–O–C); 1256 [P=O, Si(CH₃)₃]; 1963 (C=C=C). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.26 s [9H, Si(CH₃)₃], 1.33 t (3H, CH₃CH₂O, ³J_{HH} = 7.2 Hz), 1.87 m [6H, (CH₃)₂C=], 5.04 m (1H, PCH=C). ³¹P NMR spectrum (CDCl₃): δ_P 16.2 ppm. Found, %: C 47.88; H 8.02. C₁₀H₂₁O₃PSi. Calculated, %: C 48.39; H 8.47.

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as thin films. The ¹H and ³¹P NMR spectra were obtained on a Varian Unity-300 instrument at 300 and 121.42 MHz, respectively. The chemical shifts were measured relative to residual proton signals of the solvent (¹H) or 85% H₃PO₄ (³¹P, external reference).

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