## SULFENAMIDES

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Dialkyl trimethylsilyl dithiophosphites react with sulfenamides either through involvement of the trimethylsilyl group and the formation of trialkyl trithiophosphates or by isomerization of the starting silylphosphites to give S-alkyl O-trimethylsilyl alkyldithiophosphonates. The direction of the reaction depends on the nature of the substituents at the sulfur atoms of the silylphosphite and sulfenamide.

We have found that the reaction of dialkyl trimethylsilyl dithiophosphites with sulfenamides may be carried out either according to the Arbuzov reaction scheme involving the trimethylsilyl group and formation of trialkyl trithiophosphates (I) or by isomerization of the starting silylphosphites to the corresponding S-alkyl O-trimethylsilyl alkylthiophosphonates (II).



The direction of the reaction depends on the nature of the alkyl substituents at the sulfur atom of the silylphosphite and sulfenamide. In the reactions of dialkyl trimethylsilyl dithiophosphites with S-ethylsulfenamide and of diethyl trimethylsilyl dithiophosphite with S-isopropylsulfenamide, the major products are trialkyl trithiophosphates (Ia)-(Ic). However, the accumulation of isopropyl substituents in the starting compounds facilitates the formation of isomerization products (IIa)-(IIc), which may be detected in the volatile fractions of the distillation products by <sup>31</sup>P NMR spectroscopy. In the reaction of diisopropyl trimethylsilyl dithiophosphite with S-isopropylsulfenamide, isomerization with the formation of (IId) is predominant. Dialkyl trimethylsilyl dithiophosphites are stable compounds which do not isomerize in the absence of sulfenamide either upon storage or heating [1]. The reaction rate largely depends on the nature of the substituent of the sulfur atom in the sulfenamide. <sup>31</sup>P NMR spectroscopy indicated that the reaction of silyl phosphites with S-ethylsulfenamide is complete at ~20°C in 15 h, while the reaction with S-isopropylsulfenamide requires maintenance of the reaction mixtures under these conditions for more than 24 h.

## EXPERIMENTAL

The <sup>31</sup>P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz relative to 85%  $\rm H_3PO_4$ . The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz relative to TMS. The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on an MKh-1310 spectrometer.

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. 9, pp. 2146-2147, September, 1990. Original article submitted November 27, 1989. Trialkyl trithiophosphates (Ia)-(Ic). A mixture of 7.4 g (0.03 mole) diethyl trimethylsilyl dithiophosphite and 4.5 g (0.03 mole) N,N-diethyl-S-isopropylsulfenamide was maintained for 84 h at about 20°C. Fractionation gave 5.2 g (69.7%) trithiophosphate (Ib), bp 85°C (0.04 mm),  $n_D^{20}$  1.5359. PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm, J, Hz): 1.40 t (CH<sub>3</sub>C, <sup>3</sup>J<sub>HH</sub> 7.5), 1.44 d (i-CH<sub>3</sub>C, <sup>3</sup>J<sub>HH</sub> 7.0), 2.93 d.q (CH<sub>2</sub>S, <sup>3</sup>J<sub>HP</sub> 14.0).  $\delta$ P 59 ppm. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1274 (P=0), 568 (PSC). Found: C, 34.12; H, 6.97; P 12.48%. Calculated for C<sub>7</sub>H<sub>17</sub>OPS<sub>3</sub>: C, 34.42; H, 6.97; P, 12.70%.

By analogy, 11.2 g (0.04 mole) diisopropyl trimethylsilyl dithiophosphite and 5.5 g (0.04 mole) N,N-diethyl-S-ethylsulfenamide gave 8.2 g (76.6%) trithiophosphate (Ic), bp 85°C (0.03 mm),  $n_D^{20}$  1.5010,  $\delta$ P 57 ppm. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1260 (P=0), 568 (PSC). Found: C, 37.68; H, 7.42; P, 11.56; S, 37.08%. Calculated for C<sub>8</sub>H<sub>19</sub>OPS<sub>3</sub>: C, 37.21; H, 7.36; P, 12.02; S, 37.21%. Mass spectrum: [M + H]<sup>+</sup> 258.

By analogy, 10.1 g (0.04 mole) diethyldithiotrimethylsilylphosphite and 5.5 g (0.04 mole) N,N-diethyl-S-ethylsulfenamide gave 6.9 g (71.8%) trithiophosphate (Ia), bp 83°C (0.04 mm).  $n_D^{20}$  1.5655.  $\delta$ P 61 ppm [2].

N,N-Diethyltrimethylsilylamine, bp 126-128°C (750 mm),  $n_D^{20}$  1.4112 [3], was isolated in 40-60% yield from the volatile fractions of the distillation products. The products of the isomerization of the starting silylphosphites with  $\delta P$  99 ppm [(IIa) and (IIb)] and 106 ppm [(IIc)] were also detected by <sup>31</sup>P NMR spectroscopy.

S-Isopropyl O-Trimethylsilyl Isopropyldithiophosphonate (IId). A mixture of 14.0 g (0.05 mole) diisopropyl trimethylsilyl dithiophosphites and 7.6 g (0.05 mole) N,N-diethyl-S-isopropylsulfenamide was maintained for four days at about 20°C. Fractionation gave 12.3 g (89.3%) dithiophosphonate (IId), bp 125°C (10 mm),  $n_D^{20}$  1.4946. PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm, J, Hz): 1.60 d.d (CH<sub>3</sub>CP, <sup>3</sup>J<sub>HH</sub> 7.0, <sup>3</sup>J<sub>HP</sub> 25), 1.74 d and 1.77 d (CH<sub>3</sub>CS, <sup>3</sup>J<sub>HH</sub> 7.0), 2.03-2.73 m (HCP), 3.73 d.sept (HCS, <sup>3</sup>J<sub>HP</sub> 14.0), 0.70 s (CH<sub>3</sub>Si). TMS.  $\delta$ P 106 ppm. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 520, 583 (PSC), 618 (P=S), 860, 1260 (CH<sub>3</sub>Si), 1010 (POSi). Found: C, 39.68; H, 8.33; P, 11.42; S, 24.40; Si, 10.29%. Calculated for C<sub>9</sub>H<sub>23</sub>OPS<sub>2</sub>Si: C, 40.00; H, 8.52; P, 11.48; S, 23.70; Si, 10.37%. Mass spectrum: [M + H]<sup>+</sup> 271. Distillation of the volatile fractions gave 5.0 g (65.8%) starting sulfenamide, bp 45°C (10 mm),  $n_D^{20}$  1.4455.

## LITERATURE CITED

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