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LETTERS TO THE EDITOR

Reactions of Acetyl Iodide with Triethylsilylalkyl Propyl Sulfides

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We have previously shown that acetyl iodide reacts with dialkyl sulfides via cleavage of the S–C bond to give ethanethioates and alkyl iodides [1]. It was of interest to study the chemical behavior of acetyl iodide with respect to the silicon-containing dialkyl sulfides.

The previously unknown unsymmetrical triethylsilylalkyl propyl sulfides of the general formula $Et_3Si(CH_2)_nSPr$ (n = 1, 2) were chosen as starting compounds.

Triethylsilylmethyl propyl sulfide was synthesized by reacting chloromethyl(triethyl)silane with sodium propanethiolate [2].

$$Et_3SiCH_2Cl + NaSPr \xrightarrow{Et_2O,\ 7\ h} Et_3SiCH_2SPr + NaCl.$$

Triethylsilylethyl propyl sulfide was obtained by the reaction of propanethiol with vinyl(triethyl)silane under UV irradiation (irradiation source was a mercury-quartz lamp DRT-400, λ_{max} 240–250 nm) [3].

$$Et_3SiCH{=}CH_2 + HSPr \xrightarrow{h\nu,\ 10\ h} Et_3SiCH_2CH_2SPr.$$

As in the case of dialkyl sulfides, the interaction of investigated organosilicon sulfides with acetyl iodide, carried out in the solvent-free conditions at a temperature of 70–75°C for 5 h, proceeds via cleavage of the S–C bond. However, the splitting direction depends on the relative positions of the sulfur and silicon atoms. Thus, in the case of triethylsilylmethyl propyl sulfide (n = 1) triethylsilylmethyl ethanethioate and propyl iodide were identified as the reaction products. Hence, the bond between the sulfur atom and the carbon atom of propyl group is cleaved.

$$Et_3SiCH_2SPr + MeCOI \rightarrow Et_3SiCH_2SCOMe + PrI.$$

In contrast, the reaction of triethylsilylethyl propyl sulfide (n = 2) with acetyl iodide affords unexpectedly hexaethoxydisiloxane as one of the reaction products. Triethylsilylethyl ethanethioate was not found in the reaction mixture, but the formation of propyl ethanethioate was detected. This indicates that in the case of β-configuration of silicon and sulfur heteroatoms (n = 2) the bond between the sulfur atom and β-located carbon atom is cleaved to form propyl ethanethioate and triethylsilylethyl iodide. Under the reaction conditions the latter undergoes β-cleavage, which is characteristic for the β-halogenated organosilicon compounds [3]. Hydrolytic condensation of the product of this cleavage, iodotriethylsilane, occurs easily even under the influence of air moisture to give hexaethyldisiloxane.

$$Et_3SiCH_2CH_2SPr + MeCOI \rightarrow [Et_3SiCH_2CH_2I] + PrSCOMe,$$

$$Et_3SiCH_2CH_2I \xrightarrow[H_2C=CH_2]{} [EtSiI],$$

$$2EtSiI + 2H_2O \xrightarrow[H_2O]{} [Et_3Si]_2O + 2HI.$$

We assume that the specific feature of the S–C bond cleavage in the studied organosilicon sulfides is not due to the electronic factors. As expected, in all cases the acetyl group is attached to the sulfur atom, which acquires partial negative charge due to the inductive effect of substituents and electronegativity of the sulfur atom. In our opinion, the difference in the chemical behavior of triethylsilylmethyl and triethylsilylethyl propyl sulfide in the reaction with acetyl iodide is caused by the steric factors. In accordance with the mechanism of the analogous reaction of the oxygen-containing compounds [5], occurring through the formation of four-centered intermediate complex, in the case of triethylsilylmethyl propyl sulfide the steric effect of bulky triethylsilyl group will prevent the formation of such complex with the coordination center at the methyl carbon atom.

Triethylsilylmethyl propyl sulfide. To sodium mercaptide prepared from 3.9 g (51 mmol) of propanethiol and 1.8 g of sodium in diethyl ether was added 8.4 g (51 mmol) of Et_3SiCH_2Cl. The reaction was carried out at 45–55°C for 7 h. The precipitate was filtered off, washed with diethyl ether. The ether extract was evaporated, and residue was distilled in a vacuum. Yield 1.1 g (13%), bp 80°C (5 mm Hg), n_D^{20} 1.4692. IR spectrum, ν, cm^{-1}: 1695 (S–C=O), 1457 (S–CH_2), 737–763 (Si–CH_2). Found, %: C 59.16; H 11.93; S 14.24; Si 12.74. $C_{10}H_{24}SSi$. Calculated, %: C 58.82; H 11.76; S 15.69; Si 13.73.

Triethylsilylethyl propyl sulfide. A mixture of 4.3 g (57 mmol) of propanethiol and 8.0 g (57 mmol) of triethylvinylsilane was irradiated with UV light in a quartz flask with stirring for 10 h. Yield 5.1 g (55%), bp 87°C (5 mm Hg), n_D^{20} 1.4750. IR, ν, cm^{-1}: 1695 (C=O), 1249 [$\delta(CH_3)_3$–Si], 837, 757 [$(CH_3)_3$–Si]. Found, %: C 60.17; H 11.67; S 14.33; Si 12.05. $C_{11}H_{26}SSi$. Calculated, %: C 60.55; H 11.93; S 14.68; Si 12.84.

Reaction of triethylsilylmethyl propyl sulfide with acetyl iodide. A mixture of 1.1 g (54 mmol) of triethylsilylmethyl propyl sulfide and 0.9 g (54 mmol) of acetyl iodide was stirred under heating at 70–75°C for 5 h. Yield 0.7 g (35%), bp 64°C (5 mm Hg), n_D^{20} 1.4780. IR spectrum, ν, cm^{-1}: 1694 (S–C=O). Found, %: C 54.01; H 10.46; S 13.51; Si 15.54. $C_9H_{20}OSSi$. Calculated, %: C 52.94; H 9.80; S 13.73; Si 15.69. In a volatile fraction collected in the trap propyl iodide was identified by GLC and IR spectroscopy. IR spectrum, ν, cm^{-1} : 480 (CH_2I).

Reaction of triethylsilylethyl propyl sulfide with acetyl iodide. Under similar reaction conditions, from a mixture of 5.4 g (25 mmol) of triethylsilylethyl propyl sulfide and 4.2 g (25 mmol) of acetyl iodide we obtained 4.4 g (46%) of $[Et_3Si]_2O$, bp 84–87°C (5 mm Hg), n_D^{20} 1.4370 (bp 60°C (1 mm Hg), n_D^{20} 1.4340 [4]). IR spectrum, ν, cm^{-1}: 1065 (Si–O–Si). Found, %: C 58.80; H 12.17; Si 21.26. $C_{12}H_{30}OSi_2$. Calculated, %: C 58.54; H 12.20; Si 22.76. In a volatile fraction collected in the trap propyl ethanethioate was identified by GLC and IR spectroscopy. IR spectrum, ν, cm^{-1} : 1695 (S–C=O).

The IR spectra were recorded on a UR-20 spectrometer in a thin layer. Analysis of the reaction mixture by GLC was performed on a LKhM-8MDII instrument equipped with a thermal conductivity detector, carrier gas – helium, column 1000×4 mm, sorbent – Chromaton N-AW-HMDS (0.2–0.25 mm, impregnation with 5% SE-30).

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