2-(TRIALKOXYSILYLALKYLTHIO)ETHYL VINYL SULFIDES

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In order to obtain a new type of organosilicon monomers and crosslinking agents, and specifically 2-(trialkoxysilylakylthio)ethyl vinyl sulfides (I), we reacted thiols of general formula $(RO)_3Si(CH_2)_nSH$, where R = Me, and n = 1-3, with divinyl sulfide (DVS) [1].

The addition of alkanethiols to DVS was studied in detail in [2]. By analogy with [2], in order to obtain the greatest selectivity in forming the monoadduct we added the organosilicon thiols to DVS employing heat initiation and a reactant ratio of thiol: DVS = 1 : 3.

$$(RO)_3Si(CH_2)_nSH + CH_2 = CHSCH{=}CH_2 \rightarrow (RO)_3Si(CH_2)_nSCH_2CH_2SCH{=}CH_2 \quad (I)$$

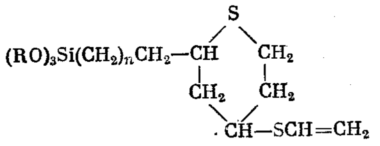
The yield of (I) reaches 75% under the optimum conditions (75-80°C, 10 h, atmospheric pressure). In vacuo (residual pressure = 35-40 mm), even at a higher temperature, the thiylation is retarded and the yield of the monoadduct drops to 53%. The trialkoxysilylalkanethiols add to DVS in the absence of a catalyst, in which connection the yield of the monoadduct is 30-40% in 24 h.

The (I) compounds are also the sole reaction products when electrophilic reagents, e.g., SO_2, are used as catalysts, which testifies to the high tendency of DVS to undergo homolytic processes.

The reactivity of the trialkoxysilylalkanethiols decreases with increase in the number of CH_2 groups that separate the S and Si atoms. This can be explained by the ability of the studied thiols to form free radicals, which decreases with increase in n. This change in the stability of the trialkoxysilylalkylthiyl radicals testifies to the electron-donor character of the $(RO)_3Si$ group.

The structure of the monoadducts was confirmed by NMR and IR spectroscopy. Thus, the NMR spectra of the (I) compounds lack the doublet of the protons of the CH_3 group and the quartet of the methylene protons of the $CH(CH_3)$ fragment, and have the multiplet of the protons of the CH_2CH_2 group (δ 2.76 ppm). The signals of the protons of the CH_2 group of the vinyl sulfide fragment are found in the regions: δ_{cis} 5.10 and δ_{trans} 5.02 ppm. The quartet downfield (δ 6.26 ppm) belongs to the = CHS grouping, $J^{trans}_{CH=CH_2} = 16$, $J^{cis}_{CH=CH} = 10$ Hz. The IR spectra of the (I) compounds have a set of frequencies of the vinylthio group in the 1585-1590 (C=C) and 3090 cm^{-1} (C–H) regions.

In contrast to the alkanethiols [2], the reaction of $(RO)_3Si(CH_2)_nSH$ with DVS proceeds with the predominant formation of the monoadducts. The diadducts $[(RO)_3Si(CH_2)_nS(CH_2)_2]_2S$ (II) can be identified only by NMR (the spectra have the signals of the protons of the following fragments: $\delta_{\rightarrow Si-CH_2}$ 0.86, δ_{S-CH_2} 2.6, $\delta_{CH_3OSi\leftarrow}$ 3.50 ppm) in the high-boiling fraction, which is formed in 10-20% yield in all of the syntheses. Based on the GLC and NMR data, this fraction represents a mixture of two compounds: adduct (II) and a compound of unestablished structure in a 70-80: 30-20 ratio. These compounds cannot be separated by distillation. By analogy with [2], it may be assumed that the unknown compound is the dimeric telomerization product with the following possible structure.



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The pure (II) adducts cannot be isolated even if excess thiol (thiol : DVS = 2 : 1) is used. Under these conditions the products are 30% of the monoadduct (I) and mainly an undistillable mixture, which apparently consists of telomers and polyorganosiloxanes. As a result, the trialkoxysilylalkanethiols add with difficulty to DVS. This conclusion is confirmed by the fact that the yields of the (II) compounds do not exceed 40-50% when the (I) compounds are reacted directly with $(RO)_3Si(CH_2)_nSH$ employing thermal initiation.

$$(RO)_3Si(CH_2)_nSH + CH_2{=}CHSCH_2CH_2S(CH_2)_nSi(OR)_3 \rightarrow (RO)_3Si(CH_2)_nSCH_2CH_2SCH_2CH_2S(CH_2)_nSi(OR)_3 \qquad \text{(II)}$$

The observed phenomenon can apparently be explained by the fact that the studied thiols are less inclined to undergo homolytic processes than the organic analogs.

EXPERIMENTAL

The NMR spectra were obtained on a Tesla BS-487B spectrometer at 80 MHz; the solvent was CCl_4 and the internal standard was TMS. The IR spectra were taken on a UR-20 spectrometer as a thin layer. The chromatographic analysis was run on a Chrom-4 instrument equipped with a katharometer, and the temperature was programmed (4 deg/min) in the range 140-285°. The column was packed with Chromaton (1.2 moles) that had been silanized with Lukoprene G-1000, and the vaporizer temperature was 260°. Freshly distilled reactants were used for the syntheses.

2-(Trimethoxysilylmethylthio)ethyl Vinyl Sulfide (Ia). A mixture of 7.9 g (0.09 mole) of DVS and 5.0 g (0.03 mole) of trimethoxysilylmethanethiol was heated in a sealed ampul for 10 h at 100-110°. Vacuum distillation gave 6.4 g (86%) of (Ia), bp 131-132° (3.5 mm): n_D^{20} 1.4986; d_4^{20} 1.1198. Found: C 38.40; H 7.11; S 24.87; Si 10.95%. $C_8H_{18}S_2SiO_3$. Calculated: C 37.72; H 7.13; S 25.20; Si 11.43%.

2-(Trimethoxysilylethylthio)ethyl Vinyl Sulfide (Ib). a) Similar to (Ia), from 6.9 g (0.08 mole) of DVS and 4.9 g (0.027 mole) of trimethoxysilylethanethiol (III) we obtained (Ib) in 67.6% yield, bp 116-117° (2.5 mm); n_4^{20} 1.4980; d_4^{20} 1.0985. Found: C 39.55; H 7.05; S 23.57; Si 10.68%. $C_9H_{20}S_2SiO_3$. Calculated: C 40.36; H 7.50; S 23.88; Si 10.83%.

b) Similar to (Ia), from 2.6 g (0.03 mole) of DVS and 5.5 g (0.03 mole) of thiol (III) we obtained (Ib) in 21.7% yield.

c) A mixture of 8.1 g (0.09 mole) of DVS and 5.7 g (0.03 mole) of thiol (III) was placed in an ampul, evacuated to a residual pressure of 35 mm of Hg, and heated at 100-110° for 10 h. Vacuum-distillation gave 4.5 g (53.7%) of (Ib).

d) A mixture of 7.8 g (0.09 mole) of DVS and 5.5 g (0.03 mole) of thiol (III) was placed in an ampul, saturated with SO_2 under cooling, sealed, and let stand at ~20° for 24 h. Vacuum-distillation gave 3 g (37.5%) of (Ib).

e) Using method d), but in the absence of SO_2, we obtained (Ib) in 37.3% yield from 6.4 g (0.075 mole) of DVS and 4.5 g (0.025 mole) of thiol (III).

f) A mixture of 8 g (0.09 mole) of DVS and 5.8 g (0.03 mole) of thiol (III) was heated in a flask for 10 h at 75-80°. Vacuum distillation gave 6.5 g (74.94%) of (Ib).

g) Using method f) we obtained (Ib) in 35.8% yield from 4.3 g (0.05 mole) of DVS and 18.2 g (0.01 mole) of thiol (III).

2-(Trimethoxysilylpropylthio)ethyl Vinyl Sulfide (Ic). Similar to (Ia), (Ic) was obtained from 7.7 g (≈ 0.09 mole) of DVS and 6.2 g (0.03 mole) of trimethoxysilylpropanethiol in a yield of 4.3 g (47.7%), bp 148-150° (3.5 mm); n_D^{20} 1.4955; d_4^{20} 1.0879. Found: C 43.13; H 7.87; S 23.06; Si 9.54%. $C_{10}H_{22}S_2SiO_3$. Calculated: C 42.52; H 7.85; S 22.69; Si 9.98%.

2,2'-Bis(trimethoxysilylethylthioethyl) Sulfide (II). A mixture of 4.2 g (0.016 mole) of 2-(trimethoxysilylethylthio)ethyl vinyl sulfide and 2.9 g (0.016 mole) of thiol (III) was heated at 80-85° for 8-10 h. Vacuum-distillation gave 3.2 g (44.4%) of (II), bp 195-200° (2 mm); n_D^{20} 1.5070; d_4^{20} 1.1669. Found: C 37.84; H 7.48; S 21.20; Si 12.55%. $C_{14}H_{34}S_3Si_2O_6$. Calculated: C 37.80; H 7.60; S 21.33; Si 12.46%.

CONCLUSIONS

Trialkoxysilylalkanethiols $(CH_3O)_3Si(CH_2)_nSH$ (n = 1-3) react with divinyl sulfide at 100-110° to give 2-(trialkoxysilylalkylthio)ethyl vinyl sulfides $(CH_3O)_3Si(CH_2)_nS\,(CH_2)_2SCH{=}CH_2$ in high yield. The reactivity of the trialkoxysilylalkanethiols decreases with increase in the number of CH_2 groups between the S and Si atoms. A second molecule of the organosilicon thiol acids adds with difficulty to divinyl sulfide to give the diadduct.

LITERATURE CITED

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USE OF $Eu(DPM)_3$ TO STUDY THE LONG-RANGE SPIN–SPIN COUPLING OF $^1H-^1H$ AND $^1H-^{14}N$ VIA THE PMR SPECTRA

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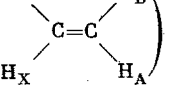
A broadening of the signals of the proton H_A 

and of the ring protons: H^2 in the spectrum of (I), and H^3 and H^4 in the spectrum of (II), is observed in the PMR spectra of the 1-vinyl derivatives of imidazole (I) and pyrazole (II) when they are recorded on BS-487C and XL-100 spectrometers (using CCl_4 or $CHCl_3$ as the solvent) at a temperature exceeding 0°C. This broadening is not removed by additional irradiation (homonuclear double resonance), but depends on the temperature. Thus, in the spectrum of (I) at −60° the width of the H_A and H_B quartets is the same, while the shape of the H^2 signal is determined by the spin–spin coupling (SSC) of the protons of the heterocycle. The above indicated broadening of the signals is not removed in the spectrum of (II) at −60°. However, in this case the lines of the H_A quartet contract under double resonance conditions when irradiation is at the H^3 frequency. This testifies to the long-range SSC of the H_A and H^3 protons ($^6J \approx 0.3$ Hz). The temperature dependence of the width of the resonance lines can indicate the effect of the quadrupole moment of the nitrogen nucleus on the relaxation of the protons via the $^1H \rightarrow {}^{11}N$ spin–spin bond. Actually, additional broadening of the H_A (Fig. 1) and H^2 signals is absent in the $^1H-\{^{14}N\}$ spectrum of compound (I). From this experiment it follows that H^2 and H^4 couple with the same nitrogen. In order to specifically establish with which nitrogen we recorded the spectrum of (I) in the presence of added $Eu(DMP)_3$. It proved that the signals of the H^2 and H^4 protons, nearest the coordination center, viz., the N-3 nitrogen [1], are respectively shifted by 1.71 and 1.65 ppm, while the signal of the nitrogen that couples with H^2 and H_A is shifted by 8.9 ppm. In the complex of pyridine (III) with $Eu(DPM)_3$ the shift (ω) of the ^{14}N signal is 1500 ppm [2], while $\omega_2 = \omega_6 = 12.16$ ppm [3], i.e., a shift in H^2 and H^6 by 1.5 ppm should correspond to a shift in ^{14}N by approximately 150 ppm. In our case the ω_N value is much smaller than the expected value, which indicates the SSC of H_A and H^2 with the N-1 nucleus. In the PMR spectrum of (II) with added $Eu(DPM)_2$, where $\omega_3 = 0.48$ ppm, the ^{14}N signal, which was assigned to the N-1 atom that couples with the H_A proton, is shifted by 8.3 ppm in a direction opposite to the ^{14}N shift in the case of (III). From the $^1H-\{^{14}N\}$ spectrum it follows that H^3 couples both with N-1 and N-2, whose signal relative to N-1 is shifted downfield by 93 ppm. When $Eu(DPM)_3$ is added this signal is shifted upfield (as in (III)) by 22.2 ppm, where $\omega_3 = 0.48$ ppm. This value is approximately three times smaller than that expected on the basis of the shift of the ^{14}N signal in the spectrum of (III). This difference can be explained by the effect of the substituent in the α position to the coordination center. It should be mentioned that the H^5 proton also couples with N-2.

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