CLEAVAGE OF α , β - AND β , γ -MONO- AND DIUNSATURATED ORGANYL ALKENYL SULFIDES BY TRIALKYL- AND TRIALKOXYSILANES

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As a continuation of studying the hydrosilylation of sulfur-containing unsaturated compounds [1] we studied the reaction of organyl alkenyl sulfides of general formula $RS(CH_2)_nCH=$ CH_2 , where $R = CH = CH_2$, n = 0 (I); $R = C_2H_5$, n = 0 (II), $R = CH_2CH = CH_2$, n = 1 (III), $R = C_2H_5$, n =4 (IV), with triethyl- and triethoxysilane in the presence of a catalyst that was obtained in situ from $(PhCN)_2PdCl_2$ and Ph_3P . This catalyst was selected because of its high efficiency and selectivity in the hydrosilylation of olefins [2, 3]. The reaction was run at 100-160°C (8-48 h) using an equimolar ratio of the reactants and a catalyst concentration of 0.00005 M.

In contrast to Pt and Rh catalysts [4], the Pd catalyst causes only the cleavage of the S-C bonds in the starting organyl alkenyl sulfides to give the corresponding Si-substituted organylthiosilanes RSSiR₃' (V) and disilthianes R₃'SiSSiR₃' (VI) (R = CH = CH₂, C₂H₅, CH₂CH = CH₂; R' = C₂H₅ (a); R' = OC₂H₅ (b). A parallel hydrosilylation was not observed for any of the studied organyl alkenyl sulfides (I)-(IV). Cleavage of the organyl alkenyl sulfides by the triethyl- and triethoxysilanes is accompanied by disproportionation of the starting silane, which leads to R₄'Si (VII) (R' = C₂H₅ (a); R' = C₂H₅ (a); R' = C₂H₅ (b).

The tendency of the S-C bond to cleave and the ratio of its cleavage products, (V) and (VI), is determined by the structure of the starting organyl alkenyl sulfide and the hydrosilylating agent. Thus, the yield of (Va) is 22%, that of (VIa) is 19%, and that of (VIIa) is 4% when equimolar amounts to (I) and $(C_2H_5)_3SiH$ are reacted in the presence of Pd catalyst for 48 h at 160°. In the case of (EtO)_3SiH the total yield of the reaction products decreases, and here the main product proves to be the disproportionation product (VIIb) (7%), while the yield of the cleavage product of the S-C bond (Vb) is only 1-2%, and (VIb) in general is not formed.

The fact that $(EtO)_3SiH$ has a much lower reactivity than Et_3SiH when reacted with organyl alkenyl sulfides is in agreement with the data given in [5, 6], where it is shown that $(EtO)_3SiH$ has the minimum reactivity when the hydrosilylation of olefins by compounds of the R_3 'SiH series is run in the presence of Pd catalysts.

When (II) is reacted with Et_3SiH , the main product is triethyl(ethylthio)silane (Va) (43% yield), and the other products are hexaethyldisilthiane (VIa) (19%) and tetraethylsilane (VIa) (5%). The reaction of triethylsilane with diallyl sulfide (III) gave mainly hexaethyldisilthiane (VIa) (38% yield), while the yield of (Va) was 15 and that of (VIIa) was 2%. Ethyl hexen-5-yl sulfide (IV), and also the saturated diethyl sulfide and aromatic diphenyl sulfide, do not react with $(C_2H_5)_3SiH$ and $(C_2H_5O)_3SiH$ under the studied conditions. In this case only disproportionation of the R₃'SiH occurs to give R₄'Si (2% yield). In contrast to this, in the presence of H₂PtCl₆·6H₂O and $[(C_6H_5)_3P]_3RhCl,$ sulfide (IV) reacts selectively with $(C_2H_5)_3SiH$ and $(C_2H_5O)_3SiH$ to give the hydrosilylation product R₃'Si(CH₂)₆SC₂H₅ (VIIIa, b). The yield of (VIIIb) when (IV) is reacted with $(C_2H_5O)_3SiH$ in the presence of H₂PtCl₆·6H₂O for $[(C_6H_5)_3P]_3RhCl$ is respectively 79 and 23%. In the case of $(C_2H_5)_3SiH$ the yield of (VIIIa) in the presence of the mentioned catalysts is only 23 and 9%.

As a result, the obtained results, in combination with our previously published data [1, 4, 7], testify to the fact that the cleavage of S-C bonds when mono- and diunsaturated organyl alkenyl sulfides are reacted with hydrosilanes proceeds only in sulfides that contain either the S-C=C or S-C-C=C grouping. This is apparently due to the fact that in sulfides of the indicated type the sulfur atom exhibits either $\pi-\sigma$ acceptor properties (vinyl sulfides) [8] or the p- π -allylic conjugation effect (allyl sulfides) [9], which leads to an increase in the electron density on the S atom and the polarity of the S-C bond.

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| | | | PLEAN | | onnd, ° | 20 | | Empirical | U U | lculate | ظ مر ا | |
|---|---------------------------------|--|------------------|----------------|----------------|----------------|----------------|--|----------------|----------------|----------------|----------------|
| Sulfide | è: | Reaction products | % | υ | н | S | s | formula | υ | н | s | Si |
| CH2=CHSCH=CH2 | C2H5 | $CH_2 = CHSSi (C_2 II_5)_3 (Va)$ $(C_2 H_5)_3SISSi (C_2 H_5)_3 (VIa)$ | 22 19 | 54,95 56,69 | 10,57 10,92 | 17,57 11,90 | 16,37 19,93 | C ₈ H ₁₈ SSi C ₁₂ H ₃₀ SSi ₂ | 55,10 54,89 | 10,40 | 18,40 12,21 | 16,10 21,39 |
| H ₂ =CHSCH=CH ₂ | C ₂ H ₅ O | $CH_{2}=CH_{3}(VIIa)$ (CH ₂ =CIISSi(OC ₂ H ₅) (V b) | 401 | | | | | | | | | |
| CH2=CHSC3H5 | C ₂ H ₅ | (C2H5SSi(C2H5) 3 (V11D) (C2H5SSi(C2H5) 3 (Va) (C2H5) 3SiSSi(C2H5) 3 (Vla) | - 6 6 | 52,02 56,05 | 11,24 11,48 | 17,64 12,43 | 16,01 19,64 | C ₈ H ₂₀ SSi C ₁₂ H ₃₀ SSi ₂ | 54,17 54,89 | 11,42 11,51 | 18,17 12,21 | 15,92 21,39 |
| .H₂=CHSC₂H₅ | C ₂ H ₅ O | (C ₂ H ₅),Si (VIIa) C ₂ H ₅ SSi(OC ₂ H ₅) ₃ (V b) | | | | | • | | | | | |
| $CH_2 = CHCH_2)_2S$ | C ₂ H ₅ | (C2H5U) (2) (VIID) CII2=CIICH2SSi (C2H5)3 (Va) (C2H5) 3SISSi (C2H5)3 (VIa) | 38 - 38 | 57,43 55,64 | 10,69 10,30 | 15,51 12,59 | 16,07 20,54 | C ₉ H ₂ 0SSi C ₁₂ H ₃₀ SSi ₂ | 57,37 54,89 | 10,70 11,51 | 17,02 12,21 | 14,91 21,39 |
| CH ₂ =CHCH ₂) ₂ S | C ₂ H ₅ O | $\begin{array}{l} (C_2H_5)_{4}Si_{1}(VIIa)\\CH_2 = CHCH_2SSi(0C_2H_5)_3(Vb)\\CH_2 = CHCH_2SSi(0C_2H_5)_3(Vb)\\CHCH_2SSi(0C_2H_5)\\CHCH_2SSi(0$ | 242 | | | | | | | | | |
| $^{\dagger}CH_2 = CH (CH_2) (SC_2H_5)$ $^{\ddagger}CH_2 = CH (CH_2) (SC_2H_5)$ | C2H5 C2H5O | (C2H5)(S1 (VII b) (C2H5)(S1 (VII b) (C2H50)(S1 (VII b) | <u>4</u> 0101 | | | | | | | | ~~ | |
| *At 100-120° for 8 | h; yie | ld of (Va) = 7%, (VIa) = | 1%, | N) (V | Ila) = | : 2%. | | | | | | |

TABLE 1. Reaction Products of Organyl Alkenyl Sulfides (R₃'SiH) with Triethylsilane and Triethoxysilane 48 h. 150-160°C

Fror H_2PtCl_6.6H_20 the yield of (C2H_5) aSi(CH_2) 6SC2H_5 (VIIIa) = 2%. 10.78%. C14H_a2Si. Calculated: C64.60; H 12.30; S 12.31; Si 10.80%. For [(C6H_5) 3P]aRhCl the yield of (VIIIa) = 23%.

 $r^{TOr} H_2PtC1_{\bullet} - 6H_2O$ the yield of $(C_2H_5O)_3Si(CH_2)_6SC_2H_5$ (VIIIb) = 23%. For $[(C_6H_5)_3P]_3RhC1$ the yield of (VIIIb) = 9%. Found: C 55.45; H 10.57; S 9.02; Si 9.26%. $C_{1_4}H_{3_2}SSiO_3$. Calculated: C 54.54; H 10.39; (VIIIb) = 9%. Found: S 10.38; Si 9.09%.

TABLE 2. Parameters of PMR Spectra of Reaction Products of Organyl Alkenyl Sulfides (I)-(IV) with Triethylsilane and Triethoxysilane

| Compound | Parameters of PMR spectra (r, ppm, J, Hz) |
|--|---|
| $ \begin{array}{c} H^2 \\ \searrow C = CHSSi(C_2H_3)_3 \\ H^4 \end{array} $ | 0,73 m (CH ₂ Si), 1,01 m (CH ₃ CSi), 5,30 (=CH ¹), 5,42 (=CH ²), 6,20 (=CH ³), ${}^{3}J_{2,3}^{\text{trans}} = 16,2, {}^{3}J_{1,3}^{\text{cis}} = 9,0$ |
| H^{2} C=CHSSi(OC ₂ H ₄); | 1,22 m (CH ₃ COSi), 3,85 q (CH ₂ O), 5,30 (=CH ¹), 5,42 (=CH ²), 6,22 (=CH ³), ${}^{3}J_{2,3}^{\text{trans}} = 16.0, {}^{3}J_{1,3}^{\text{cis}} = 9.3, {}^{2}J_{2,3}^{\text{gem}} < 0.5,$ ${}^{3}J_{\text{OCH}_{2}\text{CH}_{3}} = 7.5$ |
| $C_2H_5SSi(C_2H_5)_3$ | 0,72 m (CH ₂ Si), 1,00 m (CH ₃ CSi), 1,27 t (CH ₃ CS), 2,43 q (CH ₂ S) |
| $C_2H_5SSi(OC_2H_5)_3$ | 1,22 t (CH ₃ COSi), 1,30 t (CH ₃ CS), 2,52 q (CH ₂ S), 3,82 q (OCH ₂) |
| $\begin{array}{c} H^2 & 3 \\ \searrow C = C H C H_2 SSi(C_2 H_3)_3 \\ H^1 \end{array}$ | 0,74 m (CH ₂ Si), 0,99 m (CH ₃), 3,06 d.t (CH ₂), 4,97 m (= CH ¹) 5,2 (=CH ²), 5,76 m (=CH ³); ${}^{3}J_{2,3}^{\text{trans}} = 16,8, {}^{3}J_{1,3}^{\text{cis}} = 10,0,$ ${}^{2}J_{1,2} = 1,0, {}^{3}J_{\text{CH}_2\text{CH}_3} = 5,8, {}^{4}J_{\text{CH}_2\text{H}^2} = 1.2, {}^{4}J_{\text{CH}_2\text{H}^1} = 1,1$ |

The fact that the cleavage of S--C bonds is the sole process that is observed during the hydrosilylation of organyl alkenyl sulfides in the presence of Pd catalyst is also explained, in our opinion, by the specific traits of palladium chemistry [10-12].

The high polarity of the S-C bond in α,β - and β,γ -unsaturated organyl alkenyl sulfides facilitates the exchange processes involving Pd(II) and the subsequent reaction of the formed hypothetical complexes of RSPdCl with R₃'SiH via a four-center transition state by the following postulated scheme (the ligand is not indicated):

 $RSR' + PdCl_{2} \rightarrow RSPdCl + [R'CI]$ $RSPdCl + R_{3}'SiH \rightarrow RSPdCl - R_{3}'SiSR + [HPdCI]$ $R_{3}'Si - H$ $HPdCl - \bigvee_{RSR'} Pd(0) + HCI$ HPdCl + R'H

The catalytic character of the reaction can be explained by the repeated exchange reaction of RSR' with HPdCl due to regeneration of the $PdCl_2$ complex [13] by the equation:

$$Pd (0) + 2HCl \rightarrow PdCl_2 + H_2$$

The formation of Si-substituted disilthiane derivatives R_3 'SiSSiR_3' proceeds by an analogous scheme due to cleavage of the formed corresponding organylthiosilane derivatives R_3 'SiSR. The sequence of forming R_3 'SiSR and R_3 'SiSSiR_3' is confirmed by the effect of the reaction time and temperature on the ratio of these cleavage products. Thus, when the temperature for the reaction of ethyl vinyl sulfide (II) with triethylsilane is increased from 100-120° for 8 h to 150-160° for 48 h the ratio of the cleavage products, (Va):(VIa), changes from 7:1 to 2:1 (Table 1).

The reaction of sulfides (I)-(III) with R_3 'SiH in the presence of Pd catalyst is accompanied by much gas formation. Based on the gas chromatography data, the main component of the the mixed gaseous products, formed during the reaction of divinyl sulfide (I) with triethylsilane, is ethane. The latter is apparently the hydrogenation product of ethylene. Due to this, the amount of free hydrogen in the gas mixture proves to be very low (C₂H₆ - 68.25% and H₂ - 0.003%).

The formation of a Pd mirror on the walls of the reaction vessel is observed during the process. This is evidently due to the reduction of the Pd compounds by the R_3 'SiH, including disproportionation of the HPdCl formed during the process.

EXPERIMENTAL

For the GLC analysis we used an LMKh-8MD instrument, equipped with a katharometer as the detector, and a $1.0 \text{ m} \times 3 \text{ mm}$ column packed with 10% PMS-100 deposited on Chromaton. The temperature was programmed from 50° at a rate of 10 deg/min. The composition of the mixtures based on the chromatograms was determined by the normalization method.

The reaction mixtures were separated on a Chrom-3 instrument, using a 3.0×8 mm column packed with 10% Lukoprene G-1000 deposited on Chromaton.

The PMR spectra (Table 2) were obtained on a Tesla-487 C spectrometer (80 MHz) using 10-20% CCl₄ solutions and TMS as the internal standard.

<u>Reaction of Organyl Alkenyl Sulfides with Triethyl- and Triethoxysilane.</u> Into a glass ampul were charged $PdCl_2(C_6H_5CN)_2$ and $P(C_6H_5)_3$, and then an equimolar mixture (1:1) of the appropriate organyl alkenyl silane and either triethyl- or triethoxysilane. The ampul was sealed and heated for 48 h at 150-160° (except for the experiments where the effect of the reaction temperature and time was established).

The unreacted triethylsilane and divinyl sulfide were distilled at atmospheric pressure. On further distillation in vacuo we isolated a broad fraction with bp 35-110° (2 torr), from which we obtained all of the mentioned compounds by PGC (see Table 1).

CONCLUSIONS

Organyl alkenyl sulfides of general formula $RS(CH_2)_nCH=CH_2$ react with triethyl- and triethoxysilane in the presence of $PdCl_2(C_6H_5CN)_2$ and $P(C_6H_5)_3$, with cleavage of the S--C bond and the formation of the corresponding Si-substituted organylthiosilanes $RSSiR_3$ ' and disilthianes R_3 'SiSSiR_3'. The reaction is accompanied by the disproportionation of the starting silanes R_3 'SiH with the formation of R_4 'Si. Hydrosilylation products were not detected.

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