REACTION OF DIETHYLSILANE WITH DIALKENYL SULFIDES AS A PATH FOR THE SYNTHESIS OF HETEROCYCLIC SYSTEMS CONTAINING SILICON AND SULFUR ATOMS

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As we mentioned previously [1], H₂PtCl₆ catalyzes the addition of diethylsilane to divinyl sulfide (DVS), which leads to the formation of the isomeric α - and β -monoadducts.

 $Et_{2}SiH_{2} + CH_{2} = CHSCH = CH_{2} - \begin{pmatrix} \rightarrow Et_{2}HSiCH(CH_{3})SCH = CH_{2} \\ (I) \\ \rightarrow Et_{2}HSiCH_{2}CH_{2}SCH = CH_{2} \end{pmatrix}$

Together with addition products (I) and (II), we isolated the organosilicon cyclic compounds Et2SiCH(CH3)SCHCH3 (III) and Et2SiCH2CH2SCHCH3 (IV) which are obtained by the respective hydrosilylation of (I) and (II) [1].

A more detailed study of the reaction of Et₂SiH₂ with DVS in the presence of H₂PtCl₆ disclosed that the progress of the various reactions depends on the amount of catalyst. Thus, the use of 0.05 mole % of H2PtCl6 gives only adducts (I) and (II) in a 1.5:1 ratio. A 1.5-fold increase in the amount of catalyst causes the appearance of compounds (III) and (IV) in the reaction mixture. In addition, the hydrogenation product is also formed in harmony with the scheme

 $(I) \rightarrow Et_2HSiCH(CH_3)SCH_2CH_3$ (V)

Here the (I):(II):(III):(IV):(V) ratio is 4.6:6.9:5.2:1:2.9. However, also at this catalyst concentration the yield of products, corresponding to the initial α -addition, (I) + (III) + (V), is 1.5 times greater than the yield of the isomeric compounds (II) + (IV). At the same time, the amount of catalyst is practically without effect on the total yield of all of the reaction products, which does not exceed 25%.

The same set of compounds is also formed when 0.1 mole % of (Ph₃P)₃RhCl is used as the catalyst. Although the α -addition process also prevails in the given case, still the (I): (II):(III):(IV):(V) ratio is 5:20:7:1:16.

The fact that the hydrosilylation of DVS by diethylsilane in the presence of Pt and Rh catalysts proceeds predominantly by the Markovnikov rule is explained by the electronic structure of DVS. According to the quantum-chemical calculation [2], the β -C atom of the vinyl group of DVS has a lower electron density, which facilitates the addition of the hydride H atom of the starting silane to it.

A characteristic trait of the reaction of DVS with Et₂SiH₂ involving the Rh catalyst is the substantial yield (total of ~40%) of the hydrogenation products, and specifically ethyl vinyl sulfide (EVS) and (V). The hydrogenation processes, accompanying hydrosilyla-tion, are most probably related to the catalytic transformations of Et_2SiH_2 . In the presence of H_2PtCl_6 the latter reacts with $i-C_3H_7OH$, which is used as a solvent for the given catalyst [3]. The amount of H_2 that is liberated here is sufficient to hydrogenate the double bond in α -adduct (I). This is confirmed by the fact that when the amount of catalyst, and correspondingly i-C₃H₇OH, is increased substantially (1 ml of 0.1 M solution per 0.02 mole of Et₂SiH₂), (I) is converted completely to (V). In reactions, catalyzed by (Ph₃P)₃RhC1, the hydrogenation is apparently accomplished via the H2 that is liberated from the intermediately formed complex of Et₂SiH₂ with the catalyst [4]. Here, as was indicated previously

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[4], the diethylsilane is converted to 1,1,2,2-tetraethyldisilane. We established the presence of the latter among the reaction products of DVS with Et_2SiH_2 employing GLC.

The addition of Et_2SiH_2 to diallyl sulfide (DAS) in the presence of H_2PtCl_6 leads to the formation of two isomeric monoadducts* (total yield 20%).

 $Et_{2}SiH_{2} + (CH_{2} = CHCH_{2})_{2}S - \begin{vmatrix} \rightarrow Et_{2}HSiCH(CH_{3})CH_{2}SCH_{2}CH = CH_{2} \\ (VI) \\ \rightarrow Et_{2}HSiCH_{2}CH_{2}CH_{2}SCH_{2}CH = CH_{2} \\ (VII) \end{vmatrix}$

On the average, the (VI):(VII) ratio is 1:5. When the Rh catalyst is used, the hydrosilylation of DAS is selective and leads only to the γ -isomer (VII) (60% yield). The predominant addition of the silyl group to the terminal C atom of the double bond of DAS is in agreement with the distribution of the electron density in the allylthic group [6, 7].

A comparison of the activity of Pt and Rh catalysts in hydrosilylation reactions on the example of DVS and DAC disclosed that, on the whole, the Rh catalyst is more efficient: in its presence the reactions proceed more rapidly and with a higher yield of the products.

A similar rule is also observed for the cyclization of monoadducts (I) and (II). This is especially noticeable in the formation of the five-membered thiasilolane ring (IV), the yield of which in the case of the Rh catalyst is 48% (100°C, 12 h). Only traces of (IV) are formed under the same conditions when H_2PtCl_6 is used in the reaction. The use of a solvent (cyclohexane, 50:1 dilution) for the cyclization of (I) and (II) in the presence of H_2PtCl_6 has little effect on the yield of (III) and (IV). The heating of γ -adduct (VII) with H_2PtCl_6 (independent of the presence of a solvent) leads only to polymeric products. However, when the Rh catalyst is used, (VII) is converted in high yield (40-60%) to 5,5-diethyl-1-thia-5silacyclooctane $Et_2Si(CH_2CH_2CH_2)_2S$ (VIII).

With either the Pt or the Rh catalyst, the most inclined to form a ring is the α -isomer (I), which forms the thiasilacyclobutane derivative (III). At the same time, silacyclobutane derivatives cannot be obtained by the cyclization of diorganylsilanes of type $R_2HSi(CH_2)_nCH =$ CH_2 [8, 9]. The starting compound polymerizes when n = 1, while when n = 2, instead of the silacyclobutane derivative, only 1,1-dimethyl-1-silacyclopentane is formed. This is related to the structure of the transition state of the intramolecular hydrosilylation reaction and to the energetically unfavorable transition from the intermediate five-membered complex to the strained four-membered silacyclobutane [9]. Evidently, the smaller deformation of the CSC valence angle when compared with the CCC valence angle during transition from a linear compound to a cyclic compound facilitates the ease of forming the four-membered ring [compound (III)]. Isomer (IV), which contains a five-membered ring, is not formed when the α adduct is heated in the presence of catalyst. A similar selectivity of the process is also observed during the ring closure of the β -adduct (II), where the sole reaction product is (IV). The isomer $Et_2Si(CH_2CH_2)_2S$ is not formed under the studied reaction conditions. The intramolecular hydrosilylation of the isomeric (I) and (II) proceeds only as α -addition. In the case of (VII), ring closure proceeds only at the terminal C atom. In contrast to this, the intramolecular hydrosilylation of alkenylsilanes of type Me₂HSi(CH₂)_nCH=CH₂ in most cases leads to isomeric cyclic compounds, whose ratio depends on n [9-12]. This difference in the behavior of the alkenyl- and vinylthioalkylsilanes is caused by the presence of a S atom in the latter, and due to its π,σ -acceptor character the positive charge in organyl vinyl sulfides is concentrated on the terminal C atom [2]. The insertion of a silyl group into the vinyl sulfide molecule fails to lead to a redistribution of the electron density in the vinylthio group [13]. Consequently, during the ring closure of compounds (I) and (II) the hydride H atom, attached to the Si atom, adds to the positively charged β -C atom. The polarization of the double bond of the allylthio group, caused by the conjugation of the electron density of the vinyl group and the S atom [6], leads to a selectivity of the intramolecular hydrosilylation also in the case of the γ -adduct (VII). The structure of the obtained compounds was confirmed by the PMR spectral data.

^{*}Previously it was indicated that the reaction of DAS with diorganylsilanes in the presence of Pt/C leads only to polymeric products [5].



EXPERIMENTAL

The reaction mixtures were analyzed by GLC on a Chrom-4 instrument, equipped with a katharometer and the columns: (A) 2.4 m \times 3 mm, packed with 5% Silicone XE-60 deposited on Chezasorb, and (B) 1.2 m \times 3 mm, packed with 10% Lukoprene G-1000 deposited on Chromaton. The temperature was programmed from 80° at a rate of 4 deg/min. The composition of the mixtures was calculated by the normalization method. The preparative separation (PGC) was run on a PAKhV-07 instrument, using a 5 m \times 10 mm column packed with 15% Carbowax 20M deposited on Chromaton. The column temperature was 145°.

The PMR spectra were obtained on a Tesla BS-487 B spectrometer (80 MHz), using 10-20% CCl4 solutions and HMDS as the internal standard.

1,1,2,2-Tetraethyldisilane was synthesized as described in [14].

<u>Reaction of Diethylsilane with Divinyl Sulfide (DVS).</u> a) A mixture of 0.05 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ solution in i-PrOH and 1.76 g of Et_2SiH_2 was kept for 1 h at $^{\circ}20^{\circ}$, and then 1.72 g of DVS was added. The mixture was heated in a sealed ampul for 48 h at 100°. Vacuumdistillation gave 0.74 g of a fraction with bp 52-83° (3 mm), which contained 57% of (I) (12% yield) and 38% of (II) (8% yield). Compounds (I) and (II) were isolated from this fraction by PGC.

 $\begin{array}{l} & \quad \text{Et}_{2}\text{HSiCH}(\text{CH}_{3})\,\text{SCH}=\text{CH}_{2}\;(\text{I}),\; n_{D}^{20}\;1.4877. \ \text{Found:} \ \text{C}\;55.15;\; \text{H}\;10.38;\; \text{S}\;18.45;\; \text{Si}\;15.81\%. \\ & \quad \text{C}_{8}\text{H}_{18}\text{SiS.}\;\; \text{Calculated:} \;\; \text{C}\;55.10;\; \text{H}\;10.40;\; \text{S}\;18.39;\; \text{Si}\;16.11\%. \ \text{PMR}\; \text{spectrum}\;(\delta,\; \text{ppm}):\; 0.68 \\ & \quad \text{m}\;(4\text{H},\;\text{CH}_{2}\text{Si}),\; 1.03\;\; \text{m}\;(6\text{H},\;\text{CH}_{3}\text{CSi}),\; 1.37\;\; \text{d}\;(3\text{H},\;\text{CH}_{3}\text{CS}),\; 2.35\;\; \text{m}\;(1\text{H},\; \text{SCH}),\; 3.72\;\; \text{sext}\;(1\text{H},\; \text{SiH}),\; 5.10\;\; \text{and}\; 5.15\;\; (2\text{H},\; =\text{CH}_{2}),\; 6.28\;\; (1\text{H},\; =\text{CHS}). \;\; \text{The}\; \text{protons}\; \text{of}\; \text{the}\; \text{vinyl}\; \text{sulfide}\; \text{group} \\ & \quad \text{form a spin}\; \text{system}\; \text{of}\; \text{th}\; \text{ABC}\; \text{type.} \;\; {}^{3}\text{J}_{\text{HH}}^{\text{trans}}=16.5\;\; {}^{3}\text{J}_{\text{HH}}^{\text{cis}}=10.1\;\; {}^{2}\text{J}_{\text{HH}}^{\text{gem}}<0.2\;\; {}^{3}\text{J}_{\text{SiHCH}_{2}}= \\ & 2.8;\;\; {}^{3}\text{J}_{\text{SCHCH}_{3}}=7.2\;\; \text{Hz}. \end{array}$

Et₂HSiCH₂CH₂SCH=CH₂ (II), np^{2°} 1.4897. Found: C 54.95; H 10.39; S 18.27; Si 15.72%. C₈H₁₈SiS. Calculated: C 55.10; H 10.40; S 18.39; Si 16.11%. PMR spectrum (δ , ppm): 0.65 m (6H, CH₂Si), 0.99 m (6H, CH₃CSi), 2.75 m (2H, CH₂S), 3.72 sept (1H, SiH), 4.95 and 5.11 (2H, =CH₂), 6.29 (1H, =CHS). ³J_{HH}^{trans} = 16.5, ³J_{HH}^{cis} = 10:0, ²J_{HH}gem < 0.2 Hz.

b) After heating 10.32 g of DVS and 10.56 g of Et_2SiH_2 in the presence of 0.5 ml of 0.1 M H₂PtCl₆ solution (100°, 48 h), followed by vacuum-distillation, we obtained 4.32 g of a fraction with bp 54-87° (3 mm), which contains five components. Compounds (I)-(V) were isolated from this fraction by PGC (Fig. 1). Compound (I), 5% yield, np^{2°} 1.4880; (II), yield 7%, np^{2°} 1.4895 and $Et_2SiCH(CH_3)SCHCH_3$ (III), yield 5%, np^{2°} 1.4920. Found: C 54.30; H 10.36; S 18.14; Si 16.42%; M 174 (mass spectrum). C₈H₁₈SiS. Calculated: C 55.10; H 10.40; S 18.40; Si 16.11%. Compound (III) is a 1:1 mixture of the cis (IIIa) and trans (IIIb) isomers. PMR spectrum (δ , ppm): (IIIa), 1.35 d (6H, CH₃CS), 2.59 q (2H, CH). ³JCHCH₃ = 7.0 Hz.

Et₂SiCH₂CH₂SCHCH₃ (IV), 1% yield, nD^{2°} 1.4970. Found: C 55.06; H 10.35; S 18.05; Si 16.14%; M 174 (mass spectrum). C₈H₁₈SiS. Calculated: C 55.10; H 10.40; S 18.39; Si 16.11%. PMR spectrum (δ , ppm): 0.75 m (6H, CH₂Si), 1.05 m (6H, CH₃SiC), 1.30 d (3H, CH₃CS), 2.21 q (1H, CH), 2.79 m (2H, SCH₂), ³J_{CHCH₃} = 7.0 Hz.

Et₂HSiCH(CH₃)SCH₂CH₃ (V), 3% yield, n_D^{20} 1.4730. Found: C 54.68; H 11.26; S 18.14; Si 15.59%. C₈H₂₀SiS. Calculated: C 54.47; H 11.43; S 18.18; Si 15.92%. PMR spectrum (δ , ppm): 0.74 m (4H, CH₂Si), 1.04 m (6H, CH₃CSi), 1.25 t (CH₃CS, 3H), 1.34 d (3H, CH₃CH), 2.12 m (1H, CH), 2.47 q (2H, CH₂S), 3.69 sept (1H, SiH). ³J_{HSiCH₂} = 3.0, ³J_{CHCH₃} = ³J_{CH₃CH₂S = 7.0 Hz.} c) After heating 1.00 g of Et_2SiH_2 and 0.98 g of DVS in the presence of 11.4 mg of $(\text{Ph}_3\text{P})_3\text{RhCl}$ (100°, 24 h) the mixture contains, based on the GLC data, ethyl vinyl sulfide and compounds (I), (II), (III), (IV), (V), and 1,1,2,2-tetraethyldisilane (yield 33, 2, 8, 3, 0.5, 6, and 30%, respectively). Ethyl vinyl sulfide and the disilane were identified by comparing with authentic specimens via GLC on phases of different polarity (columns A and B).

Addition of Diethylsilane to Diallyl Sulfide. a) A mixture of 1.7 g of Et_2SiH_2 , 2.28 g of $(CH_2=CHCH_2)S$, and 0.05 ml of 0.1 M H₂PtCl₆ solution in i-PrOH was heated in a sealed ampul for 16 h at 100°. The reaction mixture contains 3% of $Et_2HSiCH(CH_3)CH_2SCH_2CH=CH_2$ (VI) and 16% of $Et_2HSi(CH_2)_3SCH_2CH=CH_2$ (VII). Vacuum-distillation gave 0.56 g of a fraction with bp 80-83° (3 mm), from which the pure (VI) and (VII) were isolated by PGC.

Compound (VI), n_D^{20} 1.4846. Found: C 59.86; H 10.40; S 14.36; Si 13.06%. C₁₀H₂₂SSi. Calculated: C 59.33; H 10.95; S 15.84; Si 13.87%. PMR spectrum (δ , ppm): 0.61 m (4H, CH₂Si), 1.00 m (6H, CH₃CSi), 1.10 m (3H, CH₃CHSi), 2.05-2.84 m (3H, SCH₂CHSi), 3.01 (2H, ==CCH₂S), 3.66 m (1H, SiH), 4.91 and 5.03 (2H, CH₂=C), 5.72 (1H, =CHCS); the protons of the allyl sulfide group form a system of the ABCX₂ type. ³J_{HH}trans = 17.5, ³J_{HH}cis = 9.5, ²J_{HH}gem = 2.0, ⁴J_{CH₂=CCH₂S = 1.0, ³J=CHCH₂S = 7.0 Hz.}

Compound (VII), n_D^{20} 1.4850. Found: C 59.75; H 11.30; S 15.00; Si 14.45%. $C_{10}H_{22}SSi$. Calculated: C 59.33; H 10.95; S 15.84; Si 13.87%. PMR spectrum (δ , ppm): 0.63 m (6H, CH₂Si), 1.03 m (6H, CH₃CSi), 1.63 m (2H, SCCH₂), 2.45 t (2H, SCH₂CCSi), 3.09 (2H, =CCH₂S), 3.71 sept (1H, SiH), 5.05 and 5.07 (2H, CH₂=C), 5.78 (1H, =CH). ³J_{HH}^{trans} = 17.5, ³J_{HH}^{cis} = 9.4, ²J_{HH}^{gem} = 2.2, ⁴J_{CH₂=CCH₂S = 1.1, ³J_{HSiCH₂} = 3.3, ³J_{SCH₂CH₂ = 7.0 Hz.}}

b) The heating of 0.75 g of Et_2SiH_2 and 0.97 g of diallyl sulfide in the presence of 8.5 mg of $(Ph_3P)_3RhC1$ (100°, 16 h) gave (VII) in 60% yield.

<u>Cyclization of α -Isomer (I).</u> a) A mixture of 1.00 g of (I) and 3 drops of Pt catalyst solution was heated for 24 h at 100°. After vacuum-distillation we isolated 0.77 g of a fraction that contained 26% of the unreacted starting compound and 74% of (III) (57% yield).

b) A solution of 1.25 g of (I) in 50 ml of cyclohexane was heated under the same conditions in the presence of 3 drops of $0.1 \text{ M} \text{ H}_2\text{PtCl}_6$ solution. The solvent was removed on a rotor evaporator. Vacuum-distillation gave 0.86 g of a fraction with bp 70-77° (4 mm), which contained 95% of (III) (65% yield).

c) After heating 0.92 g of (I) (100°, 12 h) in 15 ml of benzene in the presence of 5.2 mg of Rh catalyst the yield of (III) is 73%.

<u>Cyclization of β -Isomer (II).</u> a) The heating of 0.5 g of (II) (100°, 48 h) in the presence of 3 drops of H₂PtCl₆ solution gave (IV) in 34% yield.

b) After heating 1.1 g of (II) in 10 ml of C_6H_6 in the presence of 9.4 mg of $(Ph_3P)_3$ -RhCl (100°, 12 h) we obtained (IV) in 48% yield.

<u>Cyclization of Adduct (VII)</u>. After heating 2.70 g of (VII) in the presence of 22 mg of Rh catalyst (100°, 12 h), followed by vacuum-distillation, we isolated 1.26 g of a fraction with bp 52-55° (1.5 mm), which contained 98% of $Et_2Si(CH_2CH_2CH_2)_2S$ (VIII) (46% yield), which was purified by PGC.

Compound (VIII), n_D^{20} 1.5000. Found: C 59.75; H 11.30; S 15.00; Si 14.45%. $C_{10}H_{22}SSi$. Calculated: C 59.33; H 10.95; S 15.84; Si 13.87%. PMR spectrum (δ , ppm): 0.75 m (8H, CH₂SCH₂), 1.01 m (CH₃CSi, 6H), 1.89 m (4H, CH₂CSi), 2.70 t (4H, CH₂SCH₂). ³JSCH₂CH₂ = 6.0 Hz.

CONCLUSIONS

1. The hydrosilylation of divinyl sulfide by diethylsilane, catalyzed by H_2PtCl_6 and $(Ph_3P)_3RhCl$, is accompanied by the hydrogenation and cyclization of the obtained monoadducts. The ratio of the reaction products depends on the amount and nature of the catalyst.

2. The reaction of diethylsilane with diallyl sulfide in the presence of Pt catalyst leads to the formation of a mixture of the β - and γ -isomers. With Rh catalyst the reaction proceeds selectively in harmony with the Farmer rule.

3. The intramolecular hydrosilylation of the obtained monoadducts, containing Si-H and a double bond, in the presence of the indicated catalysts leads to compounds with either four-, five- or eight-membered rings, which contain Si and S atoms. (Ph₃P)₃RhCl is the more efficient cyclization catalyst.

4. The cyclization of the isomeric diethylvinylthioethylsilanes proceeds selectively as α -addition. Ring closure of the allylthiopropyl-substituted silane occurs at the terminal C atom of the double bond.

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