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Hydrogermylation of Silyl-substituted Ethylenes with Trimethylgermane and Trichlorogermane Etherate

V. G. Lakhtin[a], S. P. Knyazev[b], K. V. Pavlov[a], L. E. Gusel'nikov[c], E. N. Buravtseva[c], N. A. Kuyantseva[a], L. A. Parshkova[a], A. A. Mid'ko[b], V. G. Bykovchenko[a], A. V. Kisin[a], and E. A. Chernyshev[a]

[a] *State Scientific Center of Russian Federation "State Research Institute of Chemistry and Technology of Organoelemental Compounds," sh. Entuziastov 38, Moscow , 111123 Russia e-mail: eos2004@eos.inbox.ru*

[b] *Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow, Russia*

[c] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*

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Abstract—Investigation of the reaction of some vinylsilanes of the general formula $Cl_{3-n}(CH_3)_nSiCH{=}CH_2$ (n = 0,1,2,3) and 1,2-bis(trimethylsilyl)ethylene with trimethylgermane and trichlorogermane etherate was carried out. It was established that hydrogermylation only at the use of $HGeCl_3{\cdot}2Et_2O$ was sensitive to the nature of the substituting silyl groups in vinylsilanes. Nucleophilic mechanism of the reaction of trichlorogermane etherate with vinylsilanes is suggested.

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Hydrogermylation of silyl-substituted ethylenes is poorly investigated. No systematic studies of this reaction were carried out. Only several sporadic reports on the reaction of $VinSiCl_3$ [1] and $VinSiMeCl_2$ [2] with trichlorogermane and $VinSiMe_3$ with $HGeMe_3$ [2] are known.

We report here on the hydrogermylation of a series of vinylsilanes of a general formula $Cl_{3-n}(CH_3)_n{\cdot}SiCH{=}CH_2$ (n = 0, 1, 2, 3) with trimethylgermane and trichlorogermane etherate. These studies permitted the establishment of the effect of electron-donor and electron-acceptor groups in vinylsilanes on the course of the hydrogermylation and refining its mechanism. The reaction products, various 1-germyl-2-silylethanes, can be used as starting compounds for the synthesis of strained cycles, semiproducts for preparation of gas-separating membranes.

Hydrogermylation of trimethylvinylsilane **Ia**, dimethylchlorovinylsilane **Ib**, methyldichlorovinylsilane **Ic** and vinyltrichlorosilane **Id** was carried out with trimethylgermane in the presence of small amounts of H_2PtCl_6 catalyst (0.001–0.01% mass). In the absence of catalyst no reaction was observed. For example, after 10 h of reflux of a mixture of trimethylvinylsilane with $HGeMe_3$ no reaction products were found by means of GLC.

Results of the experiments in presence of H_2PtCl_6 catalyst are listed in Table 1. Hydrogermylation proceeds according to the following scheme:

$$\underset{\mathbf{I}}{Cl_{3-n}(CH_3)_nSiCH{=}CH_2} + HGe(CH_3)_3 \rightarrow \underset{\mathbf{II}}{Cl_{3-n}(CH_3)_nSiCH_2CH_2Ge(CH_3)_3}, \quad (1)$$

Ia, IIa (n = 3); **Ib, IIb** (n = 2); **Ic, IIc** (n = 1); **Id, IId** (n = 0).

Reaction (1) possesses a high selectivity. The yields of compounds **II**, derivatives of 1-germyl-2-silylethanes, attain 68–78%. The compounds obtained are prevailingly β-isomers; therefore the trimethylgermyl groups added to the most hydrogenated carbon atom. The character of the silyl substituents in vinylsilanes varying from the electron–donor Me_3Si in the compound **Ia** to the electron–acceptor Cl_3Si in the

Table 1. Yields of compounds **II**, products of reaction between $HGeMe_3$ and silyl-substituted ethylenes[a], and their properties

Compound	Yield, %	β:α isomer ratio	bp, °C (*p*, mm Hg)	n_D^{20}	^{1}H NMR spectra (group: δ, ppm)
IIa	72.5	100:0	20/1	1.4346	$-CH_2SiMe_3$ 0.63(M), $-CH_2GeMe_3$ 0.47(M), $-SiMe_3$ 0.11(S), $-GeMe_3$ 0.00(S)
IIb	78.2	100:0	60–1/11–12	1.4490	$-CH_2SiMe_2Cl$ 0.78(M), $-SiMe_2Cl$ 0.40(S), $-GeMe_3$ 0.12(S)
IIc	67.8	92.5:7.5	47/1–2	1.4590	$-CH_2SiCl_2$ 1.07(M), $-CH_2GeMe_3$ 0.78(M), $-GeMe_3$ 0.14(S), $-SiMeCl_2$ 0.76(S)
IId	73.1	94.5:5.5	38/1	1.4636	$-CH_2SiCl_3$ 1.34(M), $-CH_2GeMe_3$ 0.88(M), $-GeMe_3$ 0.17(S)

[a] In presence of 0.001–0.01 % mass of H_2PtCl_6 catalyst.

compound **Id** did not significantly affect the yield of the hydrogermylation products.

Hence, using of Me_3SiVin (**Ia**), $Me_2ClSiVin$ (**Ib**), $MeCl_2SiVin$ (**Ic**), and Cl_3SiVin (**Id**) as starting compounds we obtained 1-trimethylgermyl-2-trimethylsilylethane (**IIa**) {mass spectrum, *m/z* (I_{rel}, %): 220 $[M]^+$ (10), 205 $[M - CH_3]^+$ (18), 119 $[Me_3Ge]^+$ (79), 73 $[Me_3Si]^+$ (100)}, 1-trimethylgermyl-2-dimethylchlorosilylethane **IIb** {mass spectrum, *m/z*, (I_{rel}, %): 240 $[M]^+$ (2), 225 $[M - CH_3]^+$ (55), 119 $[Me_3Ge]^+$ (100), 93 $[Me_2ClSi]^+$ (23)}, 1-trimethylgermyl-2-methyldichlorosilylethane (**IIc**) {mass spectrum, *m/z* (I_{rel}, %): 245 $[M - CH_3]^+$ (40), 119 $[Me_3Ge]^+$ (100), 113 $[MeCl_2Si]^+$ (5)}, and 1-trimethylgermyl-2-trichlorosilylethane **IId** {mass spectrum, *m/z* (I_{rel}, %): 265 $[M - CH_3]^+$ (50), 133 $[Cl_3Si]^+$ (3), 119 $[Me_3Ge]^+$ (100).

Boiling points, refraction indices, and ^{1}H NMR spectral parameters of the compounds obtained are listed in Table 1.

Other trends were observed in the hydrogermylation of the silyl-substituted ethylenes with the trichlorogermane etherate.

In contrast to the reactions with trimethylgermane the addition of $HGeCl_3 \cdot 2Et_2O$ **III** proceeds successfully without a catalyst. Results of hydro-germylation of vinylsilanes **Ia–Id** and 1,2-bis(trimethylsilyl)ethylene **IV** with the trichlorogermane etherate are presented in Table 2.

It follows from this Table that the hydrogermylation yields the β-**V** and α-**VI** isomers, products of double germylation **VII**, and polymers.

$$\underset{\mathbf{I}}{Cl_{3-n}(CH_3)_nSiCH{=}CH_2} + \underset{\mathbf{III}}{HGeCl_3{\cdot}2\,Et_2O} \rightarrow \underset{\mathbf{V}}{Cl_{3-n}(CH_3)_nSiCH_2CH_2GeCl_3}$$

$$+ \underset{\mathbf{VI}}{Cl_{3-n}(CH_3)_nSiCH(GeCl_3)CH_3} + \underset{\mathbf{VII}}{Cl_{3-n}(CH_3)_nSiCH_2CH(GeCl_3)_2} + \text{polymers}, \qquad (2)$$

Ia, Va–VIIa (n = 3); Ib, **Vb–VIIb** (n = 2); **Ic, Vc–VIIc** (n = 1); **Id, Vd–VIId** (n = 0).

Among the products of reaction (2) compounds **V, VI**, the hydrogermylation products, present the greatest interest. Their overall yield significantly increases with the changes in the character of substituents in the initial vinylsilanes. The least yield of these compounds is observed in the reactions with vinylsilane **Ia** having the electron-donor substituent, trimehylsilyl group, and the greatest yield is characteristic of the vinylsilane **Id** having the electron-acceptor substituent, trichlorosilyl group.

Hence, hydrogermylation with $HGeMe_2$ and trichlorogermane etherate differ significantly. The yield of hydrogermylation products **IIa–IId** in the reaction with $HGeMe_3$ does not depend on the nature of substituents on the silicon atom of the starting vinylsilanes (Table 1). In contrast, the yield of hydrogermylation products **V, VI** in the reaction with trichlorogermane etherate grows in going from Me_3SiVin (**Ia**) to Cl_3SiVin (**Id**) (Table 2). This

Table 2. Reaction conditions and yields of the products in the reaction of $HGeCl_3 \cdot 2Et_2O$ with silyl-substituted ethylenes

Starting compound	Yields of the reaction products, %		
	V + VI (V:VI)	**VII**	Polymers
Ia	4.4 (83:17)[a]	4.3	62
Ib	6.2 (79:21)[a]	5.0	65
Ic	7.1 (63:37)[a]	5.8	66
Id	10.6 (100:0)[a]	5.6	77
IV	42[b]	traces[c]	–

[a] β:α isomer ratio was evaluated by ^{1}H NMR spectroscopy. [b] Compound **VIII** is formed. [c] The product of double germylation of compound **IV.**

Table 3. The energies of frontier orbitals in the starting compounds of the hydrogermylation reaction

Compound	E_{HOMO}, eV	E_{LUMO}, eV
Ia	–7.04	0.11
Ib	–7.57	–0.50
Ic	–7.97	–0.94
Id	–8.30	–1.31
III	–6.54	–0.75

increase occurs successively at the replacement of methyl groups for chlorine atom in the silyl substituent of vinylsilanes.

Hence, the increase in the yield of hydrogermylation products in going from Me_3SiVin to Cl_3SiVin is characterized (Table 2) by the following series:

$$Me_3SiVin < Me_2ClSiVin < MeCl_2SiVin < Cl_3SiVin. \quad (3)$$

In the compounds of this series successive increase in the electron-acceptor effect of the silyl substituent occurs, and hence the electron density on the double bond in this series decreases.

The established trend indicates that the hydrogermylation with trichlorogermane etherate proceeds as a nucleophilic addition of the $[GeCl_3]^-$ anion to the double bond of the olefin.

$$\equiv SiCH{=}CH_2 + [GeCl_3]^- \rightarrow [\equiv SiCH{-}CH_2GeCl_3]^-, \quad (4)$$

$$[\equiv SiCH{-}CH_2GeCl_3]^- + H^+ \rightarrow \equiv SiCH_2{-}CH_2GeCl_3. \quad (5)$$

Decrease in the electron density on the double bond in the series (3) facilitates the approach of the $[GeCl_3]^-$ ion and accelerates the rate-limiting stage (4) of the hydrogermylation. The second stage, reaction (5), is ionic and proceeds quickly.

The rule established for the series (3) agrees well with the results of quantum chemical calculations of the starting compounds that were carried out using the Gaussian 98 software[3] in the B3LYP/6-31g** approximation. The values of HOMO and LUMO energies of the vinylsilanes **Ia–Id** and trichlorogermane etherate **III** are listed in Table 3.

Analysis of the parameters of the frontier orbitals in the reacting molecules of vinylsilanes and trichlorogermane etherate shows that hydrogermylation is nucleophilic. The nucleophilic center in the etherate **III** is localized on the germanium atom.

It follows from the calculations that etherate **III** may exist in several molecular structures with close values of total energies and low potential barrier between them. One of its possible structures is close to the $GeCl_3^-$ anion coordinated with the protonated forms of diethyl ether $[GeCl_3]^- \cdot [HOEt_2]^+ \cdot OEt$. Characteristic feature of this structure is the existence of highly placed HOMO localized mainly on the germanium atom [E_{HOMO} –6.54 eV (Table 3)].

This fact shows that in the reacting system compound **III–**vinylsilanes (**Ia–Id)** the trichlorogermane is the nucleophilic agent. On the other hand, the lowest LUMO were found in the silyl-substituted olefins **Ic, Id** having electron-acceptor substituents $SiMeCl_2$ and $SiCl_3$ (Table 3). The electrophilic center is located mainly on the carbon atoms of the double bond. As seen from the data of Table 3, the LUMO energy decreases in the series:

$$Me_3SiVin > Me_2ClSiVin > MeCl_2SiVin > Cl_3SiVin. \quad (6)$$

The sequence established for the series (6) well agrees with the trend observed in the reactions under study. Hence, the reactivity and the yields of the products of hydrogermylation of the substituted vinylsilanes increase in the reversed sequence [series (3)] confirming that reaction (4) is the limiting stage of the hydrogermylation.

Alongside vinylsilanes **Ia–Id** we studied the hydrogermylation of 1,2-bis(trimethylsilyl)ethylene **IV**. It turned out that introduction of two electron-

donor $SiMe_3$ groups in the molecule of ethylene significantly affected the hydrogermylation. Compound **IV** mildly reacted with trichlorogermane etherate **III** to give 1,2-bis(trimethylsilyl)-1-trichlorogermylethane **VIII** in good yield (42%).

$$(CH_3)_3SiCH{=}CHSi(CH_3)_3 + \mathbf{III}$$
$$\mathbf{IV}$$
$$\rightarrow (CH_3)_3Si{-}\underset{\displaystyle GeCl_3}{\underset{|}{CH}}{-}CH_2Si(CH_3)_3. \qquad (7)$$
$$\mathbf{VIII}$$

Only the traces of double germylation of compound **IV** were found.

EXPERIMENTAL

The starting substances and the reaction products were analyzed on a LKhM-80 chromatograph equipped with the katharometer, stainless steel columns, 0.3 × 200 cm, stationary phase 5% mass of SE-30 silicon elastomer on Chromaton N-AW-DMCS (0.25–0.31 mm); carrier gas helium, flow rate 30 ml min^{-1}, ramp from 30 to 250°C, at the rate 12°C/min.

The identification of compounds was performed with the use of GC-MS procedure. Mass spectra were obtained on a Hewlett-Packard HP-5971 instrument, the ionizing voltage 70 V. Separation was carried out on a 0.032 × 2500 cm capillary column. DV-5 methylphenylsiloxane elastomer was used as the stationary phase, 25 μ film.

Analysis was carried out at the ramp from 50 to 280°C at a rate 7°/min, carrier gas helium, flow rate 8 ml min^{-1}. Molecular mass values are presented for the ^{28}Si, ^{35}Cl, and ^{74}Ge isotopes. ^1H NMR spectra of the compounds obtained were taken on a Bruker AM-360 Fourier spectrometer (360 MHz). Liquids were analysed as 15–30% $CDCl_3$ solutions, internal reference TMS.

Reaction of trimethylvinylsilane (Ia) with trimethylgermane. Compound **Ia**, 1.7 g, and 2.0 g of trimethylgermane were placed in a round-bottom two-necked flask equipped with a thermometer and a reflux condenser. After that two drops of a 0.01–0.001 wt % solution of H_2PtCl_6 in 2-propanol were added. After 1–2 min of the induction period the temperature of the reaction mixture increased to 140–150°C, and the process was completed in 5–7 min. Then the reaction mixture was cooled and distilled in a vacuum to give 2.7 g (72.5 g) of 1-trimethylgermyl-2-trimethylsilane, bp 20°C (1 mm Hg), n_D^{20} 1.4346 (published data bp 49.5 (13 mm Hg), n_D^{20} 1.4363 [2]). Synthesis of compounds **IIb–IId** was carried out analogously. Physicochemical properties of these compounds are listed in Table 1, and their mass spectra are presented above in the text.

Reaction of trimethylvinylsilane (Ia) with trichlorogermane etherate (III). Compound **Ia**, 4.0 g, was placed in a four-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer, and 13.1 g of compound **III** was slowly added dropwise with stirring. Spontaneous heating of the reaction mixture was observed, its temperature reached 35°C, and yellow precipitate was formed. Then the reaction mixture was heated at 50°C for 5 h. The reaction products were isolated by a vacuum distillation.

Reactions of compound **III** with the vinylsilanes **Ib–Id** were carried out analogously. In these reactions no heat evolution occurred at the addition of trichlorogermane etherate. The composition and the yields of the reaction products in the reaction of compound **III** with the vinylsilanes **Ib–Id** are presented in Table 2.

Reaction of 1,2-bis(trimethylsilyl)ethylene (IV) with trichlorogermane etherate (III). Compound **IV**, 13.8 g, was charged into a four-necked flask described above, and 26.2 g of compound **IV** was slowly added dropwise with stirring. Small heat evolution was observed (T = 35°C), and decoloration of the reaction mixture occurred. After that the mixture obtained was stirred for 5 h at 50°C. The reaction products were isolated by a vacuum distillation to give 11.8 g (42%) of 1,2-bis(trimethylsilyl)-1-trichlorogermylethane {*m/z*: 337 $[M - CH_3]^+$, 244 $[M - Me_3SiCl]^+$, 73 $[Me_2Si]^+$}. Traces of the double germylation product, 1,2-bis-(trimethylsilyl)-1,2-bis(trichlorogermyl)ethane were found. No polymer formation was observed.

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