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Abstract

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FORMATION OF UNSATURATED ORGANOSILICON COMPOUNDS IN THE REACTION OF HYDRIDOSILANES WITH OLEFINS IN THE PRESENCE OF IRON PENTACARBONYL

We have shown previously ([1]) that, in the reaction of triethylsilane with vinyl ethyl ether in the presence of $Fe(CO)_5$, an unsaturated compound of the structure $(C_2H_5)_3SiCH = CHOC_2H_5$ is formed.* In contrast to this, the reaction of silanes with olefins in the presence of iron pentacarbonyl led to the formation of saturated addition products. ([1]). A more detailed study of this question showed that, in a number of cases, the reaction between hydridosilanes and olefins in the presence of iron pentacarbonyl can proceed in two directions: according to schemes 1 and 2.

$$HSiR'R''R''' + CH_2{=}CHR \xrightarrow{Fe(CO)_5} \begin{cases} R'R''R'''SiCH_2CH_2R & (1) \\ R'R''R'''SiCH{=}CHR & (2) \end{cases}$$

It turned out that an excess of silane favors the course of the reaction according to scheme 1, while an excess of olefin favors scheme 2. Another important factor affecting the direction of the reaction is the structure of the hydridosilane; the use of methyldichlorosilane promotes the formation of saturated reaction products, whereas the use of triethylsilane favors the formation of unsaturated products.

Thus, in the reaction of triethylsilane with ethylene, at a molar ratio of the indicated reagents of 3 : 1, respectively, tetraethylsilane and a small amount of symmetrical hexaethyldisilylethane are formed in the presence of iron pentacarbonyl. Carrying out the reaction at a molar ratio of triethylsilane to ethylene equal to 1 : 5 leads to the formation of triethylvinylsilane.

We have also studied the reactions of methyldichlorosilane with ethylene, propylene, and decene-1. The indicated reactions were carried out in the presence of an excess of silane or an excess of olefin. In the case of the reaction with ethylene, as was described by us earlier ([1]), only the addition product—methylethyldichlorosilane—is formed. Upon varying the molar ratio $CH_3SiCl_2H/CH_2{=}CH_2$ from 1 : 4 to 1 : 7, we established the absence of

vinylmethyldichlorosilane in the reaction mixture. In the two other cases, mixtures of saturated and unsaturated products are formed; moreover, in the reaction of methyldichlorosilane with decene, the composition of the mixture of the unsaturated ($CH_3SiCl_2C_{10}H_{19}$) and saturated ($CH_3SiCl_2C_{10}H_{21}$) products changes little when the ratio of the initial silane and decene is changed, respectively, from 1 : 2 to 5 : 1.

In the case of the reaction of methyldichlorosilane with propylene at a molar ratio of the starting materials of 3 : 1, the resulting mixture of $CH_3SiCl_2C_3H_7$ (I) and $CH_3SiCl_2C_3H_5$ (II) contains 75% (I) and 25% (II). At a molar ratio of the starting materials of 1 : 4, the mixture contains 24% (I) and 76% (II).

Using the reaction of methyldichlorosilane with decene-1 as an example, we have shown that reactions with olefins are catalyzed only by iron pentacarbonyl—

* In the present work, the structure of this compound has been confirmed by study of the IR spectrum, rhodanation, and hydrolysis.

iron without the participation of any cocatalysts, in contrast to the reaction with acrylonitrile described by us earlier ([2]). Indeed, methyldichlorosilane and decene-1 in the presence of iron pentacarbonyl react both in sealed glass ampoules and in an autoclave, giving the same products in identical yields. Using this same reaction as an example, we established that the hydrogen acceptor in the case of the process proceeding according to scheme 2 is decene, which is thereby hydrogenated to *n*-decane.

It may be assumed that the reaction proceeds with formation of a radical or cation of the structure $CH_3SiCl_2CH_2\overset{\circ}{C}HCH_2C_7H_{15}$ (A) (where $\circ$ denotes a positive charge or an unpaired electron). On interaction with silane, species A is hydrogenated, and on interaction with an olefin it is dehydrogenated. The observed reactions may be represented, somewhat simplified, by the scheme:

$$R'R''R'''\overset{\circ}{Si} + CH_2{=}CHR \longrightarrow R'R''R'''SiCH_2\overset{\circ}{C}HR \qquad (A)$$

$$A \begin{cases} \xrightarrow{HSiR'R''R'''} R'R''R'''SiCH_2CH_2R + R'R''R'''\overset{\circ}{Si} \\ \xrightarrow{CH_2=CHR} R'R''R'''SiCH{=}CHR + CH_3\overset{\circ}{C}HR \end{cases}$$

$$CH_3\overset{\circ}{C}HR + HSiR'R''R''' \longrightarrow CH_3CH_2R + \overset{\circ}{Si}R'R''R'''.$$

Experimental Part

Reaction of triethylsilane with ethylene. With an excess of ethylene. (Preparation of triethylvinylsilane.) Into a half-liter stainless-steel autoclave were placed 34 g of $(C_2H_5)_3SiH$ and 0.5 ml of $Fe(CO)_5$. The air was displaced from the autoclave with nitrogen, after which ethylene was introduced to a pressure of 45 atm. As a result of 5-hour heating at 130°, the pressure fell from 70 to 35 atm. A total of 39.5 g of product was obtained, from which 27 g (66%

of theory) of triethylvinylsilane was isolated. After a second distillation: b.p. 144.5°; n_D^{20} 1.4330; d_4^{20} 0.7718. Found MR 47.92. For $C_8H_{18}Si$, calculated* 48.26. Literature data, see ([4]).

$C_8H_{18}Si$.	Found, %:	C 67.27; 67.39; H 12.96; 13.18
	Calculated, %:	C 67.57; H 12.75

The CRS** spectrum of the substance coincides with that described for triethylvinylsilane ([5]). The product obtained is completely soluble in conc. sulfuric acid; upon dilution of the acid, only hexaethyldisiloxane is separated (b.p. 233°, n_D^{20} 1.4328; d_4^{20} 0.8448). Found MR 75.85; for $C_{12}H_{30}Si_2O$, calculated 76.08. Literature data, see ([6]).

When this experiment was repeated, but with an initial ethylene pressure of 5 atm. (pressure drop during the reaction from 20 to 10 atm. at 130°), $(C_2H_5)_4Si$ was obtained in 73% yield of theory, calculated on the unreacted triethylsilane,*** and hexaethyldisilylethane in 20% yield.

Reaction of methyldichlorosilane with *n*-decene-1. The experiment was carried out as the preceding ones. 63 g of decene (0.45 mole), 70 g of CH_3SiCl_2H (0.6 mole), and 0.2 ml of $Fe(CO)_5$ were heated in a steel autoclave**** at 140° for 5 hr. On fractionation of the product, the following fractions were obtained: 1) 40–60°, 34 g (unreacted CH_3SiCl_2H); 2) 169–175°, 35 g; 3) 122° at 3 mm, 52 g.

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* The calculation here and below was carried out using the group increments proposed by V. F. Mironov and G. I. Nikishin ([3]).

** All spectra presented in the present work were recorded and interpreted by L. A. Leites, to whom the authors express their sincere gratitude.

*** For clarification, it should be indicated that the yields in the experiments on the interaction of ethylene with triethylsilane and triethoxysilane, reported in our previous article ([1]), refer to mixtures of all the organosilicon compounds obtained in these experiments.

**** Similar results were obtained when the reaction was carried out in sealed glass ampoules.

Fraction 2, consisting of a mixture of decene and decane, was treated with sulfuric acid. The undissolved organic layer was separated and washed. 24.1 g of a fraction with b.p. 74° at 30 mm was obtained, n_D^{20} 1.4121; d_4^{20} 0.7325. Found MR 48.52. For $C_{10}H_{22}$, calculated 48.53.

Found, %:		C 84.15; 84.15; H 15.56; 15.45
$C_{10}H_{22}$. Calculated, %:		C 84.22; H 15.58

Fig. 1

Figure 1: Fig. 1

The IR spectrum and constants coincided with the literature data.

Fraction 3, consisting of a mixture of $CH_3SiCl_2C_{10}H_{21}$ (I) and $CH_3SiCl_2C_{10}H_{19}$ (II), was redistilled. n_D^{20} 1.4571; d_4^{20} 0.9742.

Found, %:	C 52.06;	51.96;	H 8.68;	8.87;	Cl 27.34;	27.86;	Si 11.24;	11.11	
$C_{11}H_{24}SiCl_2$. Calculated, %:	C 51.76;	H 9.41;	Cl 27.83;	Si 11.00					
$C_{11}H_{22}SiCl_2$. Calculated, %:	C 52.28;	H 8.75;	Cl 28.00;	Si 11.08					

The mixture was methylated by the Grignard reaction. A fraction with b.p. 85-86°/1 mm was obtained (yield 75%). n_D^{20} 1.4390; d_4^{20} 0.7797.

Found, %:	C 73.36;	73.62;	H 13.42;	13.43;	Si 13.00;	12.89
$C_{13}H_{28}Si$. Calculated, %:	C 73.50;	H 13.18;	Si 13.21			
$C_{13}H_{30}Si$. Calculated, %:	C 72.81;	H 14.10;	Si 13.09			

Fig. 1

In the Raman spectrum of the trimethyl derivative obtained, in the region of the frequencies of the C=C bond, two lines were found: 1615 cm^{-1} and a band at 1662-1670 cm^{-1} split into 2 components. From this it may be concluded that the substance is apparently a mixture of $Me_3SiCH{=}CH{-}C_8H_{17}$ (III) and $Me_3SiCH_2CH{=}CHC_7H_{15}$ (IV). Evidence for the presence of III is the line at 1615 cm^{-1} (for a compound of the type $R_3SiCH{=}CHCH_3$, 1620 cm^{-1}) ([7]). Evidence for the presence of IV is the split band at 1662-1670 cm^{-1}, and the line at 1155 cm^{-1} present in the spectrum, characteristic of compounds containing a double bond in the β-position to silicon ([8]). The splitting of the band at 1662-1670 cm^{-1} is probably connected with the presence of cis- and trans-isomers ([8,9]).

On the basis of the yield obtained, calculated from *n*-decane, the content of unsaturated compounds in the mixture studied is 73%, according to the equation

$$CH_3SiCl_2H + 2C_{10}H_{20} \rightarrow CH_3SiCl_2C_{10}H_{19} + C_{10}H_{22}.$$

Treatment of this mixture with conc. sulfuric acid showed that the substance studied consists of a saturated product insoluble in sulfuric acid ($\sim$ 40%) and an unsaturated compound soluble in sulfuric acid ($\sim$ 60%). Upon dilution of the

sulfuric-acid layer with water, only hexamethyldisiloxane is isolated, b.p. 97–99°, n_D^{20} 1.3750; d_4^{20} 0.7676.

Found MR 48.43. For $C_6H_{18}Si_2O$ calculated 49.02. For literature data, see ([6]). It should be noted that, upon treatment of a mixture of $CH_3SiCl_2C_{10}H_{21}$ and $CH_3SiCl_2C_{10}H_{19}$ with sulfuric acid, partial decomposition of the saturated silane occurred, since on fractionation of the residue insoluble in sulfuric acid, n-decane was isolated.

Reaction of methyldichlorosilane with propylene. From 60 g of CH_3SiCl_2H (0.52 mole), 84 g of C_3H_6 (2 moles), and 1 ml of $Fe(CO)_5$, 40 g of a fraction with b.p. 124–130°, n_D^{20} 1.4380; d_4^{20} 1.0553, was obtained.

Found %: C 30.99; 30.97; H 5.58; 5.58; Si 17.91; 17.63; Cl 45.45; 45.44
$C_4H_8SiCl_2$. Calculated %: C 30.98; H 5.19; Si 17.09; Cl 45.83
$C_4H_{10}SiCl_2$. Calculated %: C 30.59; H 6.42; Si 17.85; Cl 45.15

After methylation with a Grignard reagent, a fraction with b.p. 87–88°, n_D^{20} 1.4042; d_4^{20} 0.7147, was obtained.

Found %: C 62.68; 62.83; H 12.92; 12.86
$C_6H_{14}Si$. Calculated %: C 63.08; H 12.35
$C_6H_{16}Si$. Calculated %: C 61.98; H 13.87

In the Raman spectrum of the trimethyl derivative, lines were found that are characteristic of $(CH_3)_3SiCH = CHCH_3$ ([7]) and $(CH_3)_3SiCH_2CH_2CH_3$ ([10]).

Treatment with conc. sulfuric acid showed that the mixture contains 25% saturated silane with b.p. 87–88°, n_D^{20} 1.3950; d_4^{20} 0.7050. Found MR 39.53. For $C_6H_{11}Si$ calculated 39.49.

Found %: C 62.53; 62.59; H 14.02; 14.20
$C_6H_{16}Si$. Calculated %: C 61.98; H 13.97

For literature data, see ([11]).

The IR spectrum coincides with that of an authentic $(CH_3)_3SiCH_2CH_2CH_3$.

Upon dilution of the sulfuric-acid layer with water, only hexamethyldisiloxane was isolated.

The presence of unsaturated compounds in the mixture under study is also confirmed by the results of rhodanation. The rhodanometric bromine number found was: after 1 hour 63.5, after 24 hours 98. Calculated for $(CH_3)_3SiC_3H_5$, 140.3. The content of unsaturated compounds in the mixture studied is 70%.

Investigation of the structure of $(C_2H_5)_3SiCH = CHOC_2H_5$ (V). For V the rhodanometric bromine number found was: after 5 min 85.7; after 0.5 hour 97.4; after 1 hour 109.5. Calculated 85.9. The observed increase in the rhodanometric bromine number is apparently associated with side reactions. Acid hydrolysis of V was carried out by treatment with a sulfuric-acid solution of

2,4-dinitrophenylhydrazine. Acetaldehyde hydrazone was obtained, m.p. 146° (from alcohol).

Found %: N 25.19; 25.09. For $C_8H_8N_4O_4$ calculated %: N 24.99. The IR spectrum of V was recorded on an IKS-14 (Fig. 1). Splitting of the double-bond band into two components, 1597 and 1609 cm^{-1}, is characteristic of simple vinyl ethers and has been observed previously ([12–14]). The authors explain this phenomenon by rotational isomerism.

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