## REACTIONS OF HYDRIDE SILANES WITH SUBSTITUTED ACETYLENES IN PRESENCE OF IRON CARBONYLS\*

N. A. Kuz'mina, E. Ts. Chukovskaya, ard R. Kh. Freidlina

As shown earlier [1],  $\alpha$ -olefins react with hydride silanes in presence of iron pentacarbonyl with formation of the corresponding organosilicon addition product and a mixture of unsaturated organosilicon compounds differing in the position of the double bond in the alkenyl group. Simultaneously there occur the hydrogenation of the olefin and its isomerization with migration of the double bond along the molecular chain [1, 2]. The main courses of this reaction can be expressed by the scheme:

 $\begin{array}{c|c} \text{HSiX}_3 + \text{CH}_2 = \text{CHR} \xrightarrow{\text{Fe}(\text{CO})_5} & \xrightarrow{\text{A}} \text{X}_3 \text{SiCH}_2 \text{CH}_2 \text{R} \\ \hline & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & & \\ & &$ 

The direct formation of alkenylsilanes in the reaction of hydride silanes with olefins has no analogy in the chemistry of organosilicon compounds. It is interesting that the course of the reaction is affected by the nature of the metal carbonyl. It is known [3] that, unlike iron pentacarbonyl, dicobalt octacarbonyl initiates only the addition of the hydride silane to the olefin and the isomerization of the olefin. In this case the formation of the unsaturated organosilicon compound and the accompanying hydrogenation of the original olefin [course B in scheme (1)] do not occur.

The mechanism of the reaction studied, which comprises the addition of the hydride silane at the double bond, the formation of the unsaturated organosilicon compound, and the hydrogenation and isomerization of the original unsaturated compound, is obviously extremely complicated. A number of observations show that these reactions are not free-radical processes. In the first place, no telomer-homologs are formed as a result of the reaction. In the second place, the reaction is sensitive to polar effects. Thus, with unsaturated compounds  $CH_2 = CHR$ , in which R is an electron-donor substituent (Alk, OAlk), reaction goes readily, but, when R is an electron-acceptor substituent (R=CN, COOR), reaction does not go [4]. It is interesting that in the case of the reactions of thiols with olefins catalyzed with iron penta-carbonyl the reverse relation applies: the process goes readily with acrylic compounds, but does not go with  $\alpha$ -olefins [5]. This is probably to be explained by the opposite polarities of the bonds Si-H and S-H. In the third place, unlike the reactions of hydride silanes with olefins in presence of peroxides, in which trichlorosilane reacts most readily and trialkylsilanes least readily, the reaction in presence of iron pentacarbonyl goes just as readily with trialkylsilanes as with trichlorosilane. In the fourth place, it has been shown [6] that iron pentacarbonyl is able to initiate reactions whose heterolytic character does not give rise to doubt, namely, the alkoxylation of trialkylsilanes with ethers.

On the basis of all these facts we have expressed the view that the reactions of hydride silanes with olefins catalyzed by iron pentacarbonyl are not free-radical processes. It was of interest to extend this reaction to compounds with a triple bond, because this may provide new information about the sphere of application and preparative significance of the reaction and about its mechanism.

In the present work we have investigated the reactions of diethylmethylsilane with 1-pentyne, 5decyne, and diphenylacetylene in presence of iron pentacarbonyl or diiron nonacarbonyl. It was found that the behavior of aliphatic acetylenes in this reaction is extremely similar to the behavior of olefins. Thus, the reaction goes only with  $\alpha$ -acetylenes. For example, under the conditions studied iron pentacarbonyl does not initiate the reaction of trialkylsilane with 5-decyne.

The reaction of 1-pentyne with diethylmethylsilane goes in a complicated way: a mixture of organosilicon compounds of composition  $CH_3(C_2H_5)_2SiC_5H_{8\pm 1}$  was obtained in about 40% yield. It was shown by

\*This article is published in accordance with a resolution of the Conference of Editors-in-Chief of Journals of the Academy of Sciences of the USSR of July 12, 1962, as a dissertation paper by N. A. Kuz'mina.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1272–1277, June, 1967. Original article submitted December 7, 1966.

Starting substances	Contents of isomers, %			
	in initial mixture		in reaction product	
	cis	trans	cis	trans
$\begin{array}{l} CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5}\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + (C_{2}H_{5})_{3}SiH\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5} + (C_{2}H_{5})_{3}SiH\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5}\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5}\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5} + (C_{2}H_{5})_{3}SiH\\ CH_{3}(C_{2}H_{5})_{2}SiCH = CHC_{3}H_{7} + Fe(CO)_{5} + (C_{2}H_{5})_{3}SiH\\ \end{array}$	0 0 64 64 64	100 100 100 36 36 36	0 0 19 35 62 54	100 100 81 65 38 46

TABLE 1. Isomerization of cis- and trans-Diethylmethyl-1-pentenylsilanes

means of gas-liquid chromatography (GLC) that this mixture consisted of at least six substances. Among these, by comparison with known synthetic samples, we identified cis- and trans-diethylmethyl-1-pentenyl-silanes. It was shown that diethylmethylpentylsilane, which could be formed by the hydrogenation of these alkenylsilanes, was not present in the reaction mixture. According to its Raman spectrum, this fraction did not contain alkenylsilanes with a terminal double bond. The fraction contained a vinyl (relative to the position of the silicon atom) double bond (1617 cm<sup>-1</sup>), an allyl double bond (1661 cm<sup>-1</sup>), and triple bonds of two types (2173, 2214 cm<sup>-1</sup>). The Raman spectra were determined with an ISP-51 instrument with a medium camera.

Hence, like the reactions of hydride silanes with olefins, the reaction of diethylmethylsilane with 1-pentyne in presence of iron pentacarbonyl led to the formation of both addition products  $CH_3(C_2H_5)_2SiC_5H_9$ , containing a pentenyl group, and also dehydrogenation products  $CH_3(C_2H_5)_2SiC_5H_7$ , containing a pentynyl group. By means of GLC in the reaction mixture we found, apart from unchanged pentyne, also pentane, 1-pentene, and cis- and trans-2-pentenes in an amount of about 13 moles per cent. In the reaction of 1-pentyne with diethylmethylsilane a considerable amount of high-boiling substances were also formed, and these were not investigated more closely. The IR spectrum of this fraction contains a frequency characteristic for a C = O group.

To check whether migration of the double bond occurs in the alkenylsilanes formed under the conditions of the reaction, we carried out the following experiments. cis- and trans-Diethylmethyl-1-pentenylsilanes were heated with iron pentacarbonyl, with triethylsilane, and with a mixture of these two substances. As will be seen from the table, the trans isomer does not change under the action of iron pentacarbonyl or triethylsilane. Only in presence of both these substances did partial isomerization of the trans isomer into the cis isomer occur (by 19%). Under the same conditions the cis isomer is not isomerized under the action of triethylsilane; in presence of iron pentacarbonyl or a mixture of triethylsilane and iron pentacarbonyl partial isomerization of the cis isomer into the trans isomer occurs (by 50%). Migration of the double bond along the alkenyl chain did not appear to occur.

Interesting results were obtained in the investigation of the reactions of diethylmethylsilane with diphenylacetylene and with cis- and trans-stilbenes in presence of iron pentacarbonyl. We supposed that the reaction of the hydride silane with diphenylacetylene should go in the most simple fashion. In the first place, diphenylacetylene is incapable of isomerization. In the second place, the product of the addition of

a silvl group to diphenylacetylene  $C_{6}H_{5}$ -C=C- $C_{6}H_{5}$ , whatever the form of the transition state may be, does  $| \begin{array}{c} | \\ X_{8}Si \end{array}$ 

not contain hydrogen atoms in the  $\alpha$ -position relative to the silvl group and is therefore incapable of dehydrogenation. This makes possible an unequivocal solution of the question of whether the hydrogenation of the original unsaturated compound is possible only at the expense of the hydride silane, or whether the participation of hydrogen eliminated in the formation of the unsaturated organosilicon compound is essential for this process. Actually, in presence of iron pentacarbonyl diphenylacetylene reacts with diethylmethylsilane with formation of the adduct (1,2-diphenylvinyl)diethylmethylsilane in 93% yield. By means of GLC we found only a small amount (less than 1%) of trans-stilbene and bibenzyl in the reaction mixture, i.e., hydrogenation of the diphenylacetylene does not occur to an appreciable extent. This shows that under conditions under which the formation of a dehydrogenated organosilicon compound is impossible, the accompanying hydrogenation of the original unsaturated compound does not occur either. Under the conditions studied we also did not observe the hydrogenation of the main reaction product (1,2-diphenylvinyl)diethylmethylsilane, which is shown by a comparison of the NMR spectra and of the chromatographic retention times of independently synthesized (1,2-diphenylvinyl)diethylmethylsilane and the product of the reaction of diphenylacetylene and diethylmethylsilane. The reaction of diphenylacetylene with diethylmethylsilane is also of interest from the point of view of the stereochemistry of the addition of hydride silanes to diphenylacetylene. As shown in [7, 8], the sterochemistry of the addition of hydride silanes to acetylenes depends on the nature of the catalyst: thus, in presence of  $H_2PtCl_6 \cdot 6H_2O$  cis addition occurs.

The NMR spectra of the adducts which we obtained with use of iron pentacarbonyl and  $H_2PtCl_6 \cdot 6H_2O$  as catalysts proved to be identical. In the NMR spectra, determined with a Hitachi H-60 instrument, there are two groups of multiplets. The Si-alkyl groups give signals in the typical region  $0.3 \le \delta \le 1.3$  with an integral intensity of 13 units. The protons of the phenyl nuclei give a typical weakly split multiplet with its center at  $\delta \approx 7.10$ . The C-H proton has a chemical shift of 6.85. The total intensity of signals in this region is 11 units. Hence, in the case of reaction catalyzed by iron pentacarbonyl cis addition again occurs.

Attempts to bring about the addition of dichloromethylsilane to diphenylacetylene with the use of peroxide catalysis (benzoyl peroxide, t-butyl peroxide, dicyclohexyl peroxydicarbonate) were unsuccessful. This shows that diphenylacetylene does not react appreciably with hydride silanes under free-radical conditions.

It is interesting that neither cis- nor trans-stilbene forms an organosilicon compound when heated with diethylmethylsilane in presence of iron pentacarbonyl. Under the experimental conditions used cisstilbene is partially isomerized into trans-stilbene. When cis-stilbene is heated with iron pentacarbonyl under the same conditions, but in absence of the silane, isomerization does not occur.

It is known [9] that diiron nonacarbonyl catalyzes certain reactions (e.g., the isomerization of the double bond in olefins) at lower temperatures than iron pentacarbonyl. With the reactions of diethylmethyl-silane with diphenylacetylene and with 1-pentene as our examples we found that in presence of diiron pentacarbonyl the same products are formed as when iron pentacarbonyl is used, but reaction can be brought about at lower (by 40-50°) temperatures.

Passing to an examination of the results obtained in the present investigation, we must mention that they are not fully in accord with the scheme orginally proposed [6]. Thus, on the basis of this scheme it is difficult to explain the stereospecificity of the addition of diethylmethylsilane to diphenylacetylene and also the presence in the products of the reaction of diethylmethylsilane with 1-pentyne of a diethylmethylpentenylsilane with a double bond in the allyl position relative to the silicon atom.

According to the literature, iron pentacarbonyl forms stable complexes with acetylene and particularly with diphenylacetylene [10, 11]. Less stable complexes of iron carbonyls with olefins are also known [12]. There are also isolated references to the existence of compounds containing an Fe-Si bond [13]. Analogous compounds with a Co-Si bond have been described recently [3]. All this allows us to suggest that under the conditions of our reactions intermediate complexes of iron carbonyls are formed with participation of both the unsaturated compound and the hydride silane.

## EXPERIMENTAL

<u>Reaction of Diphenylacetylene with Diethylmethylsilane.</u> Under the Action of <u>Iron Pentacarbonyl.</u> A glass ampule was charged with 50 mmoles of diphenylacetylene, 100 mmoles of diethylmethylsilane, and 0.9 mmole of iron pentacarbonyl. After cooling the mixture, evacuating the ampule, and displacing the air with argon, we sealed the ampule and heated it in a thermostat at 160° for 7 h. Excess of diethylmethylsilane was distilled from the reaction mixture, and the residue was vacuum-fractionated. We obtained a 93% yield of (1,2-diphenylvinyl)diethylmethylsilane; b.p. 138° (0.4 mm);  $n_D^{20}$  1.5755;  $d_4^{20}$  0.9725. Found: C 81.57, 81.45; H 8.67, 8.65; Si 10.30, 10.25%; mol. wt. 280.5, 314.7. C<sub>19</sub>H<sub>24</sub>Si. Calculated: C 81.30; H 8.62; Si 10.00; mol. wt. 296.4.

By means of GLC (glass column, length 2 m, diameter 4 mm; Chromosorb W, 0.25-0.50 mm; stationary phase 5% silicone elastomer; thermal conductivity detector; carrier gas helium; temperature 180°) we showed that, apart from (1,2-diphenylvinyl)diethylmethylsilane and a little unchanged diphenylacetylene, the reaction mixture contained cis- and trans-stilbenes in an amount not exceeding 1-2%. In special experiments it was shown that under these conditions cis-stilbene and bibenzyl are not separated. By chromatography on a column of length 4 m and diameter 4 mm with a solid phase of celite and a stationary phase of polyethylene glycol (8°) at 180° we showed that bibenzyl was present in the mixture (less than 1%).

<u>Under the Action of Diiron Nonacarbonyl.</u> By procedure analogous to that of the preceding experiment at 100° from 18 mmole of diphenylacetylene, 33 mmoles of diethylmethylsilane, and 0.23 mmole of diiron nonacarbonyl we obtained 11.2 mmoles (62%) of (1,2-diphenylvinyl)diethylmethylsilane.

Under the Action of  $H_2PtCl_6 \cdot 6H_2O$ . Three drops of a 10% solution of  $H_2PtCl_6 \cdot 6H_2O$  in isopropyl alcohol were added to a mixture of 17.4 mmoles of diphenylacetylene and 27.4 mmoles of diethylmethyl-silane, and the mixture was refluxed for 5 h. The reaction mixture was vacuum-fractionated; we isolated a 90% yield of a substance with b.p. 135-138° (0.4 mm);  $n_D^{20}$  1.5720;  $d_4^{20}$  0.9707. Found: C 80.86, 80.94; H 8.74, 8.57; Si 9.77, 9.99%.  $C_{19}H_{24}Si$ . Calculated: C 81.30; H 8.62; Si 10.00%.

The adducts obtained were shown to be identical by the identities of their retention times in chromatography under the conditions described for the first experiment, and also by the identities of their IR and NMR spectra.

In Presence of Peroxides. The experiment was conducted by the procedure described for the first experiment. A mixture of 19 mmoles of diphenylacetylene, 38 mmoles of dichloromethylsilane, and 1.1 mmoles of t-butyl peroxide was heated in a sealed ampule at 140° for 5 h. The product contained only 5% of chlorine (calculated for the adduct 24.2%) and was mainly unchanged diphenylacetylene. Analogous results were obtained when the reaction was conducted in presence of benzoyl peroxide (100°, 5 h) and dicyclohexyl peroxydicarbonate. In the last case the reaction was conducted in an open vessel at  $57^\circ$ .

<u>Preparation of (1,2-Diphenylethyl)diethylmethylsilane</u>. By the hydrogenation of (1,2-diphenylvinyl)diethylmethylsilane over freshly reduced palladium (5%) on barium sulfate in an absolute ethanol medium we obtained a 70% yield of (1,2-diphenylethyl)diethylmethylsilane;  $n_D^{20}$  1.5465;  $d_4^{20}$  0.9663. Found: C 81.07, 81.05; H 9.29, 9.40; Si 9.77, 9.40%; MR 92.64.  $C_{19}H_{26}Si$ . Calculated: C 80.77; H 9.27; Si 9.93%; MR 92.39.

<u>Reactions of cis- and trans-Stilbenes with Diethylmethylsilane in Presence</u> of Iron Pentacarbonyl. The experiment was conducted by the procedure described for the above experiment with iron pentacarbonyl. The substances taken for reaction were cis-stilbene (2.4 mmoles), diethylmethylsilane (2.4 mmoles), and iron pentacarbonyl (0.1 mmole). It was shown by means of GLC under the conditions described above that the reaction mixture did not contain products of the reaction of stilbene with the hydride silane; under the conditions of the experiment cis-stilbene was isomerized into trans-stilbene to the extent of 76%. When 5 mmoles of cis-stilbene was heated with 0.26 mmole of iron pentacarbonyl under the same conditions, no isomerization occurred. trans-Stilbene was not isomerized into cis-stilbene in analogous experiments.

Reaction of 1-Pentyne with Diethylmethylsilane in Presence of Iron Pentacarbonyl. The experiment was conducted by the above-described procedure. The substances taken for reaction were 1-pentyne (0.16 mole), diethylmethylsilane (0.16 mole), and iron pentacarbonyl (2.2 mmoles). The residue remaining after starting substances had been distilled from the reaction mixture was vacuum-distilled. In a yield of 38 moles per cent we obtained fraction I:  $CH_3(C_2H_5)SiC_5H_{8 \pm 1}$ , b.p. 99-104° (70 mm);  $n_D^{20}$  1.4445;  $d_4^{20}$  0.7840. Found: C 70.48, 70.60; H 12.88, 12.89; Si 16.75, 16.73%; MR 58.15.  $C_{10}H_{22}Si$ . Calculated: C 70.50; H 13.02; Si 16.47%; MR 57.63.  $C_{10}H_{20}Si$ . Calculated: C 71.13; H 11.94; Si 16.67%.

By means of GLC (glass column, 6 m in length and 4 mm in diameter; solid phase 13% of 3,3'-oxydipropionitrile; detection by thermal conductivity; temperature 98°) it was shown that the product was a mixture of sila hydrocarbons (there were six peaks on the chromatogram), of which by comparison with known synthetic samples we identified cis- and trans-diethylmethyl-1-pentenylsilanes. trans-Diethylmethyl-1-pentenylsilane is one of the main reaction products.

From the reaction mixture we also isolated a fraction with b.p.  $70-90^{\circ}$  (1 mm), which amounted to 51% of the weight of fraction I. For the investigation of the hydrocarbon part of the reaction mixture the experiment was conducted in 5-ml ampules with subsequent chromatography of the reaction mixture on a column of length 6 m and diameter 4 mm (solid phase brick; stationary phase 13% of diethylene glycol dibutyrate; detection by thermal conductivity; temperature  $42^{\circ}$ ). As reference substance for the quantitative

determination of pentane we used hexane (without a correction factor). It was found that pentane and cisand trans-2-pentenes are formed in an amount not exceeding 13 moles per cent on the 1-pentyne taken.

Reaction of 5-Decyne with Diethylmethylsilane in Presence of Iron Pentacarbonyl. The experiment was conducted by the procedure described for the first experiment. The substances taken for reaction were 5-decyne (49.3 mmoles), diethylmethylsilane (49.3 mmoles), and iron pentacarbonyl (0.8 mmole). The 5-decyne was recovered unchanged; the reaction scarcely wentatall.

Isomerization of cis- and trans-Diethylmethyl-1-pentenylsilanes under the Action of Iron Pentacarbonyl. By the addition of dichloromethylsilane to 1-pentyne in presence of benzoyl peroxide with subsequent ethylation of the dichloromethyl-1-pentenylsilane we obtained a mixture of cis- and trans-diethylmethyl-1-pentenylsilanes, b.p. 91° (35 mm). Found: C 69.89; H 12.94; Si 16.23%.  $C_{10}H_{22}Si$ . Calculated: C 70.50; H 13.02; Si 16.47%. By means of GLC (as described above) we showed that the substance obtained contained 64% of cis- and 36% of trans-diethylmethyl-1pentenylsilanes.

trans-Diethylmethyl-1-pentenylsilane was prepared by the addition of diethylmethylsilane to 1pentyne in presence of  $H_2PtCl_6 \cdot 6H_2O$  by the procedure described in [7, 8]; it was identical in retention time to the trans-diethylmethyl-1-pentenylsilane obtained as an admixture in the synthesis of cis-diethylmethyl-1-pentenylsilane.

The isomerization experiments were conducted in sealed ampules in an atmosphere of argon. The amounts taken were 2 mmoles of cis- or trans-diethylmethyl-1-pentenylsilane, 2.5 mmoles of triethyl-silane, and 0.15 mmole of iron pentacarbonyl. The ampules were heated at 160° for 7 h. The reaction mixtures were investigated by means of GLC (for chromatography conditions see experiment with 1-pentyne). The results of the experiments are given in the table.

All the NMR, IR, and Raman spectra were determined and interpreted by L. A. Leites, É. I. Fedin, and R. G. Gasanov, whom we thank.

## CONCLUSIONS

1. The reaction of diethylmethylsilane with 1-pentyne in presence of iron pentacarbonyl leads to a complex mixture of diethylmethylpentenylsilanes and diethylmethylpentynylsilanes. Simultaneously, part of the pentyne taken is hydrogenated with formation of pentenes and pentane.

2. Diethylmethylsilane adds to diphenylacetylene in presence of iron pentacarbonyl or diiron nonacarbonyl with close to quantiative yield of the adduct. The reaction goes stereospecifically as a cis addition, and it is not complicated by the hydrogenation of the diphenylacetylene. It is concluded that the hydrogenation of the original unsaturated compound is dependent on the dehydrogenation of the intermediate product of the addition of the silyl group to the unsaturated compound.

3. On the basis of the behavior of cis- and trans-diethylmethyl-1-pentenylsilanes, taken as an example, it was shown that under the conditions of the reaction studied isomerization with migration of the double bond along the molecular chain does not occur.

## LITERATURE CITED

- 1. R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao-i, and A. N. Nesmeyanov, Dok. AN SSSR, <u>132</u>, 374 (1960).
- 2. E. Ts. Chukovskaya, N. A. Kuz'mina, and M. I. Rozhkova, Zh. obshch. khimii, 36, 2170 (1966).
- 3. J. F. Harrod and A. J. Chalk, J. Amer. Chem. Soc., 87, 1133 (1965).
- 4. R. Kh. Freidlina, Tsao-i, and E. Ts. Chukovskaya, Dokl. AN SSSR, 132, 149 (1960).
- 5. R. Kh. Freidlina, R. G. Petrova, E. Ts. Chukovskaya, and I. A. Kuz'mina, Summaries of Papers Presented at the Symposium "Structure, Reactivity, and Mechanisms of Reactions of Compounds with Multiple Bonds and Small Rings" [in Russian], Izd. "Khimiya," (1967), p. 49.
- 6. R. Kh. Freidlina, N. A. Kuz'mina, and E. Ts. Chukovskaya, Izv. AN SSSR, Ser. khim., 1966, 176.
- 7. R. A. Benkeser and R. A. Hicker, J. Amer. Chem. Soc., 80, 5290 (1958).
- 8. R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Surcher, J. Amer. Chem. Soc., <u>83</u>, 4385 (1961).
- 9. T. A. Manuel, J. Organ. Chem., 27, 3941 (1962).

- 10. H. W. Sternberg, R. Markby, and J. Wender, J. Amer. Chem. Soc., <u>80</u>, 1009 (1958).
- 11. W. Hübel and E. H. Braye, J. Inorgan. Nucl. Chem., 10, 250 (1959).
- 12. E. K. von Gustorf, M. C. Henry, and C. D. Pierro, Z. Naturforsch., 21, 42 (1966).
- 13. B. J. Aylett and J. M. Campbell, Chem. Comm. No. 11, 218 (1965).