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Contributions to the Chemistry of Silicon and Germanium. XII.[1] The Transformation of Disilane, Trisilane, and *n*-Tetrasilane with Elementary Bromine and Chlorine in Freon

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A short time ago, the reaction of iodine with silanes was described.[1] For the first time a controlled reaction of disilane (Si_2H_6), trisilane (Si_3H_8), and *n*-tetrasilane (n-Si_4H_{10}) with elementary bromine and chlorine has been realized. The halogenation of silanes with bromine and chlorine proceeds smoothly at low temperatures in highly dilute solution. By this process large quantities of silanes can easily be halogenated. The mono- and disubstituted bromo- and chlorosilanes, most of which were unknown up to now, were separated by gas chromatography and examined by nmr spectroscopy.

Introduction

Silanes react extremely violently, often explosively, when mixed with elementary bromine or chlorine even at low temperatures.[2,3] When mixed with iodine, though, they react smoothly at −30° according to the equation[1]

$$>\mathrm{SiH} + \mathrm{I_2} \longrightarrow >\mathrm{SiI} + \mathrm{HI}$$

The cleavage of the Si–Si bond cannot be neglected.

$$>\mathrm{Si{-}Si}< + \mathrm{I_2} \longrightarrow 2>\mathrm{SiI}$$

The separation of the iodosilanes SiH_3–$SiHI_2$ and SiH_2I–SiH_2I is difficult on account of the iodosilanes SiH_2I_2 and $SiHI_3$.[1]

Up to now halogenated silanes were usually prepared by treating silanes with HCl or HBr, respectively, in the presence of aluminum bromide or aluminum chloride as catalysts[4]

$$>\mathrm{SiH} + \mathrm{HX} \xrightarrow{\mathrm{AlCl_3}} >\mathrm{SiX} + \mathrm{H_2} \quad (\mathrm{X} = \mathrm{Cl, Br})$$

As this reaction proceeds in the gaseous phase, this method is not suitable for the preparation of halogenides of trisilane or of the higher silanes. Furthermore, the removal of the aluminum halogenide catalyst is difficult. Lately mono- and disilanes were chlorinated by silver chloride[5]

$$>\mathrm{SiH} + 2\mathrm{AgCl} \longrightarrow >\mathrm{SiCl} + \mathrm{HCl} + 2\mathrm{Ag}$$

Bromosilanes could be prepared from mono- and disilanes and boron tribromide[6]

$$6>\mathrm{SiH} + 2\mathrm{BBr_3} \longrightarrow 6>\mathrm{SiBr} + \mathrm{B_2H_6}$$

We treated disilane, trisilane, and *n*-tetrasilane at low temperature with elementary bromine and chlorine according to

$$>\mathrm{SiH} + \mathrm{Br_2} \longrightarrow >\mathrm{SiBr} + \mathrm{HBr}$$
$$>\mathrm{SiH} + \mathrm{Cl_2} \longrightarrow >\mathrm{SiCl} + \mathrm{HCl}$$

We could show that the Si–Si bond in disilane is not cleaved by chlorine and bromine. Trisilane and *n* tetrasilane cleaved in a small amount.

By highly diluting the halogen and silane we achieved a nonexplosive reaction. Thus the reaction proceeds smoothly at −80°. Low-boiling Freons, such as CCl_3F (bp +23.8°) and CCl_2F_2 (bp −29.6°), were used as solvents for the starting materials. The halogen solution was added into the silane solution by means of a dropping funnel fitted with a dewar jacket to cool the halogen solution to −80°. We found it suitable to dilute each component 15-fold.

Experimental Part

The silanes were prepared by decomposition of a large amount of magnesium silicide (Mg_2Si) with aqueous sulfuric acid. The pure silanes were separated from the crude mixture which had been first formed by fractional distillation.[7] The disilane was kept in a steel cylinder with a pressure valve at room temperature; trisilane and *n*-tetrasilane were kept in glass flasks at −80°.[8]

All experiments were conducted in an atmosphere of dry nitrogen. We used the formerly described working technique,[9] with rubber caps,[10] protective tubes, hypodermic needles, "needle bridges,[11] and syringes (with a tightly fitting rubber piston). A high-vacuum apparatus was used which was equipped with ground joints for reaction flasks, a mercury gauge (which worked at the same time as an overpressure valve), and a pure nitrogen inlet. Oxygen was removed by evacuating five times and flushing with pure nitrogen.

During our first experiment with a 30% chlorine solution, a violent explosion occurred. We therefore point out that the reaction proceeds relatively riskless, when the solution is sufficiently diluted (1:15). However, when these experiments are run, asbestos gloves, asbestos clothing, and a protective face helmet should be worn. During the experiment the operator stood behind a bulletproof shield 2 m from the reaction apparatus.

The silanes were dissolved (1:15) in Freon R 12 (CF_2Cl_2, bp −29.6°). The Freon was freed from oxygen and water by

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(1) Part XI: F. Fehér, P. Plichta, and R. Guillery, *Chem. Ber.*, **103**, 3028 (1970).

(2) A. Stock and C. Somieski, *Ber. Deut. Chem. Ges.*, **50**, 1739 (1917).

(3) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, **76**, 4631 (1954).

(4) A. Stock and C. Somieski, *Ber. Deut. Chem. Ges.*, **53**, 759 (1920).

(5) R. P. Hollandsworth and M. A. Ring, *Inorg. Chem.*, **7**, 1735 (1968).

(6) J. E. Drake and J. Simpson, *Inorg. Nucl. Chem. Lett.*, **2**, 219 (1966).

(7) F. Fehér, G. Kuhlbörsch, and H. Luhleich, *Z. Anorg. Allg. Chem.*, **303**, 283 (1960); F. Fehér and H. Fischer, *Naturwissenschaften*, **51**, 461 (1964).

(8) We refer to prior publications in this series of papers.

(9) F. Fehér, G. Kuhlbörsch, and H. Luhleich, *Z. Anorg. Allg. Chem.*, **303**, 294 (1960); F. Fehér, G. Kuhlbörsch, ann H. Luhleich, *Z. Naturforsch.*, **14b**, 466 (1959).

(10) "Insulinkappen" or "Penicillinkappen" of Messrs. Biotest, Frankfurt/Main, Germany.

(11) A "needle bridge" consists of a thin steel tube (about 1-mm diameter) with sharpened ends. The needle bridge was used for transfusing larger amounts of liquids from one flask to another one under nitrogen. This operation was accomplished by producing a slight overpressure in the flask containing the liquid to be transfused whereas normal pressure was maintained in the other flask.[9]

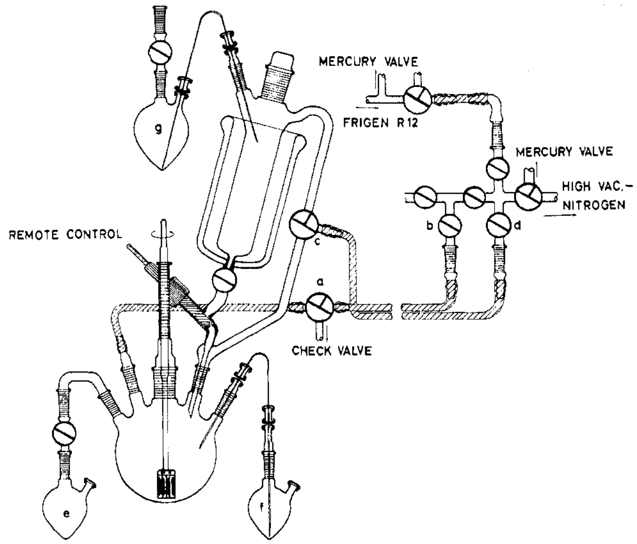

Figure 1.—Reaction apparatus.

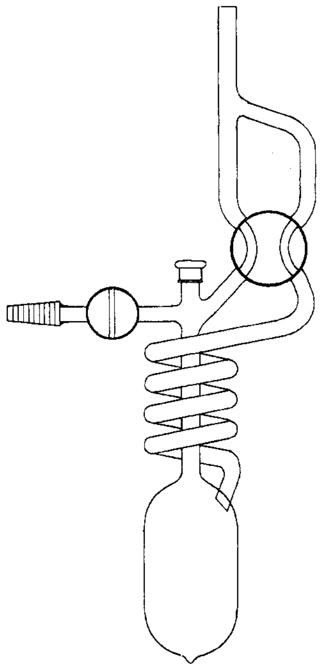

Figure 2.—Fraction collector for the preparative gas chromatography. The samples of 0.5 or 1.0 cm^3 were injected using argon-flushed syringes. The rubber cap of the protective tube fitted into the inlet of the injection block.

alkaline pyrogallol solution and concentrated sulfuric acid. Chlorine and bromine were weighed as liquids and diluted (1:15) with Freon R 11 ($CFCl_3$, bp +23.8°). The halogen–Freon solution was freed from oxygen by freezing at −196° and melting under high vacuum (during the melting the dissolved gases escaped from the liquid), followed by flushing with pure nitrogen. This procedure was repeated twice.

The reaction apparatus (Figure 1) consisted of a round-bottomed flask fitted with an airtight stirrer, a dropping funnel, and a tubing joint leading to the high-vacuum unit. The dropping funnel had a high-vacuum tight Teflon cock, which could be worked from behind the protective shield by way of a flexible tube 2 m long. Thus the dropping funnel need not be opened by hand in order to avoid injuries in case of explosion. Also behind the protective shield was a three-way cock (a) which could be connected with the reaction flask as well as with the high-vacuum unit. The third end of the three-way cock (a) leads to a back-pressure valve (not drawn) which dipped into water. The reaction flask was connected by a curved pipe to a supply flask (e) into which the formed halogen silanes could be distilled. Through the distillation the low-boiling halogen silanes were roughly separated from the high-boiling ones, in order to facilitate gas chromatographic separation.

The silane (disilane, trisilane, or *n*-tetrasilane) was transferred into the flask by means of a "needle bridge" from (f) (disilane after cooling to −80°), and then a 15–20-fold volume quantity of Freon R 12 was condensed onto the silane under slight underpressure. The chlorine or bromine solution was transmitted through a "needle bridge" from (g) into the dropping funnel which was cooled to −80°. (The bromo solution was cooled to −10° only.) During the halogenation a small stream of nitrogen was maintained, which escaped through the back-pressure valve (a). By this way, any developing hydrogen chloride (bp −85°) was removed. Hydrogen chloride and hydrogen bromide dissolve very easily in water so that an underpressure could arise in the apparatus. Thus the pressure was observed permanently at the check valve and the mercury valve.

After the reaction, the mixture was allowed to warm at room temperature and the hydrohalogenic acid and the solvents were evaporated with an aspirator. The formed halogen silanes were then condensed into flask (e); during this operation the curved pipe had to be heated.

Gas chromatography separations of the obtained reaction mixtures were run on a Hewlett-Packard Model 775 Prepmaster. The preparative column was 2 m × 1 in., 20% silicon oil on Chromosorb GAW, 60–80 mesh. The fraction collector is shown in Figure 2.

The following quantities were allowed to react. Chlorination of disilane was performed with 20 ml (14 g, 0.22 mol) of disilane and 25.0 g (0.348 mol) of chlorine. Chlorination of trisilane was performed with 14.0 g (0.152 mol) of trisilane and 18.0 g (0.250 mol) of chlorine. Bromination of disilane was performed with 14 g (0.22 mol) of disilane and 55.0 g (0.344 mol) of bromine. Bromination of trisilane was performed with 14.0 g (0.152 mol) of trisilane and 40.0 g (0.250 mol) of bromine. Bromination of *n*-tetrasilane was performed with 10.5 g (0.086 mol) of *n*-tetrasilane and 16.0 g (0.100 mol) of bromine (see Figures 3–7).

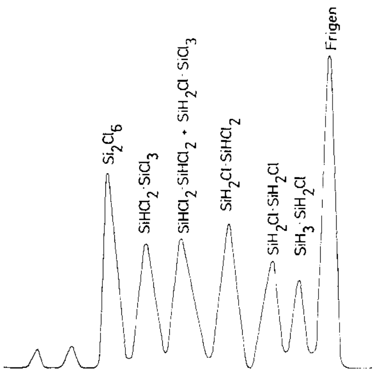

Figure 3.—Gas chromatogram of the reaction mixture from the chlorination of disilane: SiH_3SiH_2Cl, 0.95 g ≃ 6.7%; SiH_2ClSiH_2Cl, 1.96 g ≃ 13.8%; $SiH_2ClSiHCl_2$, 2.93 g ≃ 20.7%; $SiHCl_2SiHCl_2$ + $SiH_2ClSiCl_3$, 2.96 g ≃ 20.9%; $SiHCl_2SiCl_3$, 2.18 g ≃ 15.4%; Si_2Cl_6, 3.21 g ≃ 22.6%; separated chlorides, 14.19 g ≃ 100%. Column temperature 60–180°; heating rate 5°/min; gas stream 0.5 l./min.

Results and Discussion

The prepared bromo- and chlorosilanes were examined by nmr spectroscopy. Samples were dissolved in C_6D_6 with TMS as an internal standard. Chemical shifts of the obtained substances are as follows: SiH_2Cl-SiH_2Cl, singlet, τ 5.47 ppm; $SiH_2ClSiHCl_2$, triplet, τ 4.63

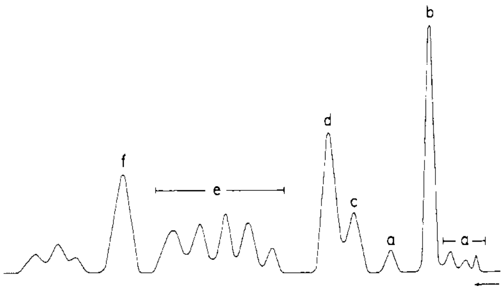

Figure 4.—Gas chromatogram of the reaction mixture from the chlorination of trisilane: (a) unknown substances; (b) trisilane; (c) $SiH_3SiHClSiH_3$, 1.55 g = 16.4%; (d) $SiH_3SiH_2SiH_2Cl$, 3.12 g = 33.0%; (e) and (f) higher chlorides of trisilane, 4.79 g = 0.6% (separated chlorides, 9.47 g). Column temperature 60–200°; heating rate 3.8°/min; gas stream 0.5 l./min.

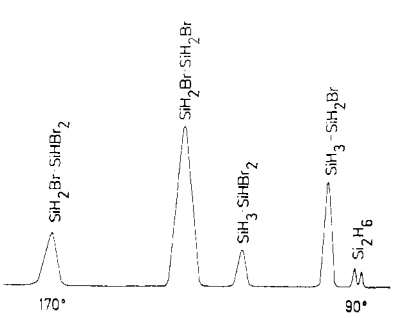

Figure 5.—Gas chromatogram of the reaction mixture from the bromination of disilane: SiH_3SiH_2Br, 3.37 g = 6.6%; SiH_3SiHBr_2; SiH_2BrSiH_2Br, 48.23 g = 86.3%; $SiH_2BrSiHBr_2$, 3.94 g = 7.1% (separated bromides, 55.44 g). Column temperature 85–200°; heating rate 5°/min; gas stream 0.5 l./min.

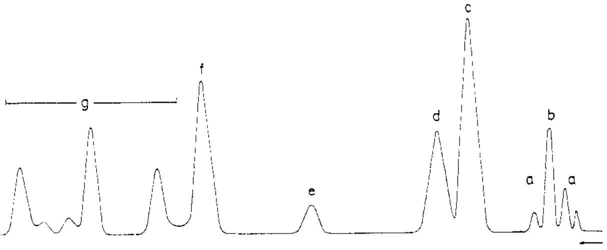

Figure 6.—Gas chromatogram of the reaction mixture from the bromination of trisilane: (a) unknown substances; (b) trisilane, 1.82 g; (c) $SiH_3SiHBrSiH_3$, 4.38 g = 43.1%; (d) $SiH_3SiH_2SiH_2Br$, 1.83 g = 18.0%; (e) and (g) unknown substances; (f) $SiH_3SiHBrSiH_2Br$, 3.98 g = 38.9% (separated bromides, 10.19 g). Column temperature 90°–190°; heating rate 3.8°/min; gas stream 0.5 l./min.

ppm, doublet, τ 5.55 ppm, relative intensity 2:1; $SiHCl_2SiHCl_2$, singlet, τ 4.68 ppm; $SiH_2ClSiCl_3$, singlet, τ 5.45 ppm; $SiHCl_2SiCl_3$, singlet, τ 4.78 ppm, ^{29}SiH coupling J = 293 Hz; $SiH_3SiH_2SiH_2Cl$, triplet, τ 5.30 ppm ($-SiH_2Cl$), multiplet, τ 6.84 ppm ($-Si_2H_5$), relative intensity 5:2; $SiH_3SiHClSiH_3$, septet, τ 5.12 ppm ($-SiHCl$), doublet, τ 6.67 ppm ($-SiH_3$), relative intensity 6:1, HH vicinal coupling J = 3.2 Hz; SiH_2BrSiH_2Br, singlet, τ 5.93 ppm, ^{29}SiH coupling J = 233 Hz; $SiH_2BrSiHBr_2$, triplet, τ 4.60 ppm, doublet, τ 5.64 ppm, relative intensity 2:1, HH vicinal coupling J = 2.7 Hz; $SiH_3SiH_2SiH_2Br$, multiplet, τ 5.80 ppm ($-SiH_2Br$), multiplet, τ 6.68 ppm ($-Si_2H_5$), relative intensity 5:2; $SiH_3SiHBrSiH_3$, could not be isolated in pure form, therefore no usable spectrum could be obtained; $^4SiH_3{}^3SiH_2{}^2SiH_2{}^1SiH_2Br$, triplet, τ 5.58 ppm ($-^1SiH_2Br$), quintet, τ 6.40 ppm ($-^2SiH_2-$), relative intensity 7.6:2, multiplet with a sharp signal at 6.57 ppm ($^4SiH_3{}^3SiH_2-$), ^{29}SiH coupling of SiH_2Br J = 112 Hz; $^4SiH_3{}^3SiH_2{}^2SiHBr{}^1SiH_3$, sextet, τ 5.54 ppm ($-^2SiHBr-$), doublet, τ = 6.33 ppm ($^1SiH_3-$), relative intensity 8.8:1, doublet, τ 6.55 ppm; this doublet is overlapped by a multiplet ($^4SiH_3{}^3SiH_2-$); ^{29}SiH coupling of $^1SiH_3-$ J = 102 Hz.

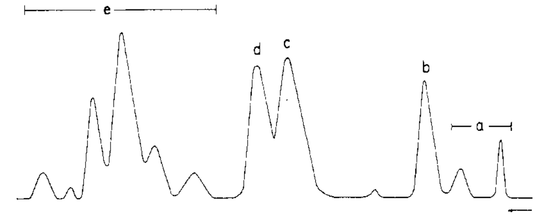

Figure 7.—Gas chromatogram of the reaction mixture from the bromination of *n*-tetrasilane: (a) unknown substances; (b) *n*-tetrasilane; (c) $SiH_3SiH_2SiHBrSiH_3$, 1.92 g = 51.8%; (d) $SiH_3SiH_2SiH_2SiH_2Br$, 1.78 g = 48.2%; (e) higher bromides of *n*-tetrasilane (separated bromides, 3.70 g). Column temperature 90–200°; heating rate 5°/min; gas stream 0.6 l./min.

Bromo- and chlorosilanes rearrange after some time. All the prepared bromo- and chlorosilanes are subject to self-ignition and are sensitive to humidity. At normal pressure liquid silanes burn only in the presence of air. Contrary to this, chlorosilanes are dangerous, as they tend to spontaneous explosion on contact with the smallest traces of air.

Mass spectra were recorded of the chloro- and bromosilanes. Typical examples for a chloro- and a bromosilane follow.

$SiHCl_2SiCl_3$.—The 70-eV spectrum of $SiHCl_2SiCl_3$ exhibits the most abundant peak of the molecular ion group at *m/e* 234. The isotope pattern corresponds to that calculated for five chlorine atoms. Typical fragment ions arrive from the loss of one chlorine ($Si_2Cl_4H^+$) as well as from cleavage of the central bond in $SiCl_3^+$ (*m/e* 133) and $SiCl_2^+$ (*m/e* 98).

n-$SiH_3SiH_2SiH_2SiH_2Br$.—The isotope pattern of the molecular ion group (most abundant peaks at *m/e* 200 and 202) is consistent with the presence of a bromine and four silicon atoms. Loss of the SiH_3 group results in the formation of $Si_3H_6Br^+$ (*m/e* 169 and 171).