

Preparation of Some Organic Silicon Hydrides

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The preparation of the following nine silanes from the corresponding ethoxysilanes is described: di- and tripropylsilane, di- and tributylsilane, mono-, di-, and triamylsilane, monohexylsilane and diphenylsilane. Reductions were carried out with lithium aluminium hydride either directly or after treatment with aluminium chloride. Densities, refractive indices, and molecular refractivities are given.

As in this laboratory a number of alkylethoxysilanes were available, it was desired to use them for preparation of the corresponding alkylsilanes by substituting the ethoxygroups with hydrogen. An attempt to reduce tri-*n*-propylethoxysilane with lithium aluminium hydride dissolved in diethyl ether, was not successful. If, however, lithium aluminium hydride and the ethoxysilane were mixed without a solvent and heated to about 100° for two hours, tri-*n*-propylsilane was obtained in 75—80 % yield. Reductions were also carried out in dibutyl ether at the same temperature, but the yields were not appreciably improved. Thus, tri-*n*-amylethoxysilane was reduced both without solvent and in dibutyl ether. The yield was 78 and 80 % respectively.

The methods just described were found to be unsatisfactory for the preparation of *n*-amylsilane, because polymerisation occurred, decreasing the yield to about 30 %.

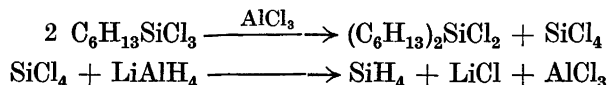
Voronkov, Dolgov, and Dimitrieva¹ have reported that trialkylhalogen-silanes can be prepared by distillation of disiloxanes or octaethyltrisiloxane from aluminium halides. I have tried a similar but modified method, where mono-, di-, and trichlorosilanes probably are intermediates. The ethoxysilane was mixed with aluminium chloride without any solvent present. When the reaction which then occurred was complete, the reaction mixture was dissolved in diethyl ether. This solution was decanted from precipitate, if any, and then introduced dropwise into a stirred slurry of lithium aluminium hydride in diethyl ether. Spontaneous reaction occurred giving the desired alkyl silanes. By this method it was possible to prepare *n*-amyl- and *n*-hexylsilane in yields of 65—70 %.

It seems not to be necessary to use more than one third of a mole of aluminium chloride per ethoxy group. Tri-*n*-butylsilane was prepared from alumi-

nium chloride and tri-*n*-butylethoxysilane in the molar ratios 1 : 1 and 1 : 2.7. In both cases the yield was about 70 %.

Except for the case that three ethoxygroups, bonded to silicon, are reduced, this method has no advantage over the direct reduction first described.

When alkyltriethoxysilanes were reduced by this method small amounts of gas were formed. They were presumed to be silane. This can easily be explained as a rearrangement of intermediate alkyltrichlorosilane in the presence of aluminium chloride², giving small amounts of dialkyldichlorosilane and silicon tetrachloride, the latter of which on reduction gives silane, *e.g.*



In order to suppress this reaction prolonged heating with aluminium chloride should be avoided. Regarding the risk of spontaneous ignition, it is recommended to carry out the reductions in an atmosphere of nitrogen.

The reaction products were isolated in two different ways.

1. The reaction mixture was rapidly filtered and the solvent was carefully removed by distillation. After cooling at room temperature and standing for some hours, two layers were formed. Sometimes the lower layer solidified on prolonged standing. The upper layer, which contained the silane, was distilled. In some cases, particularly when the silanes could be distilled at moderate temperatures, separations of the layers were not achieved, but the silicon hydrides were distilled directly from the mixture, sometimes at reduced pressure.

The silanes isolated in this way were washed first with 5 *N* hydrochloric acid, then twice with water, dried with calcium chloride and finally redistilled.

2. After filtration the reaction mixture was hydrolysed by dropwise addition to an excess of ice-cooled 5 *N* hydrochloric acid in a three-necked flask fitted with reflux condenser, dropping funnel and mechanical stirrer. When hydrolysis was completed the silane was separated, washed twice with water, dried with calcium chloride and distilled. This method of isolation must be used for diphenylsilane (see the experimental part). For the alkylsilanes method 1 is preferable.

When studying the substitution of ethoxy groups by propyl groups in methylethoxysilanes with the aid of propylmagnesium chloride³, a reduction, similar to those described here, was once observed. Thus methyltriethoxysilane and *n*-propylmagnesium chloride on heating to 150° yielded some methyl-di-*n*-propylsilane together with the expected methyltri-*n*-propylsilane and methyl-di-*n*-propylethoxysilane.

EXPERIMENTAL

Silicon analyses, refractive indices, densities and molecular refractivities are given in Table 1. The molecular refractivities found refer to the Lorenz-Lorentz formula. For the alkyl groups the bond refractivities given by Smith⁴, and for the silicon-hydrogen bonds the value 3.20 given by Warrick⁵ were used to obtain the calculated molecular values.

Table 1. Physical constants and analyses.

Substance	B.p. °C	Pres- sure mm	n_D^{20}	d^{20}	MR _D		% Si	
					found	calc.	found	calc.
(<i>n</i> -C ₂ H ₅) ₃ SiH ₂	111 ^a	760	1.4111	0.7205	40.08	40.09		
(<i>n</i> -C ₃ H ₇) ₃ SiH	171 ^b	760	1.4284	0.7601	53.63	53.73		
(<i>n</i> -C ₄ H ₉) ₃ SiH ₂	160 ^c	760	1.4241	0.7458	49.38	49.36		
(<i>n</i> -C ₄ H ₉) ₃ SiH	104 ^d	12	1.4380	0.7793	67.50	67.63		
<i>n</i> -C ₅ H ₁₁ SiH ₂	86	748	1.4042	0.7019	35.62	35.71	27.6	27.5
(<i>n</i> -C ₅ H ₁₁) ₂ SiH ₂	81	12	1.4324	0.7636	58.62	58.64	16.3	16.3
(<i>n</i> -C ₅ H ₁₁) ₂ SiH	147	17	1.4436	0.7894	81.54	81.54	11.4	11.6
<i>n</i> -C ₆ H ₁₃ SiH ₂	112	760	1.4131	0.7189	40.35	40.35	24.3	24.2
(C ₆ H ₅) ₃ SiH ₂	125 ^c	11	1.5802	1.0027	61.19	61.26	15.0	15.2

Boiling points reported in literature: ^a 111° ⁴, ⁵; ^b 170° ⁶; ^c 160° ⁴; ^d 86–87° at 2.5 mm⁷; ^c see text. The amylsilanes and hexylsilane do not appear to have been published before.

A. Reduction of ethoxy groups with lithium aluminium hydride without solvent

Tri-n-amylsilane. 28.6 g (0.1 mole) of tri-*n*-amylethoxysilane and 1.9 g (0.05 mole) of lithium aluminium hydride were mixed in a 100 ml round bottomed flask. A slow spontaneous reaction began and the temperature rose to 40°. The mixture was heated for two hours to about 100°. After cooling, the reaction mixture was extracted with anhydrous ether and filtered in a dry atmosphere. The ether was withdrawn, and distillation yielded 19.0 g (78 %) tri-*n*-amylsilane boiling at 144–146° (14 mm).

Tri-n-propylsilane was prepared in the same way from 10.0 g (0.05 mole) tri-*n*-propyl-ethoxysilane and 1.0 g (0.026 mole) lithium aluminium hydride. The yield was 6.4 g (81 %) tri-*n*-propylsilane b.p. 59° (13 mm).

Diphenylsilane was prepared from 12.8 g (0.047 mole) diphenyldiethoxysilane and 2.4 g (0.063 mole) lithium aluminium hydride. Isolation was achieved by hydrolysis with 75 ml hydrochloric acid according to method 2 described above. Distillation yielded 5.8 g (67 %) diphenylsilane boiling at 124–126° (11 mm). West and Rochow⁴ have reported the boiling point 97° at 13 mm for diphenylsilane which does not seem to be correct.

In another experiment with the same amounts of starting materials the ether was distilled off after filtration as described for triamylsilane. A solid was left behind which did not distil, and no diphenylsilane could be isolated by distillation. When, however, the solid was dissolved with 5 *N* hydrochloric acid while cooling with ice the diphenylsilane was liberated and two phases were formed, which were separated. The upper one weighed 7.1 g (0.039 mole) and contained almost exclusively diphenylsilane. The lower aqueous phase was analysed for metals and was found to contain no lithium, but 1.19 g (0.044 g atoms) of aluminium, determined as alumina. Thus the solid compound contained about one gram atom of aluminium per gram atom of silicon. (The fact that the silicon aluminium compound on hydrolysis with hydrochloric acid gave only a silicon dihydride and an aluminium salt might indicate that the crystalline compound contained aluminium silicon bonds.) Diphenylsilane was also prepared from diphenyldichlorosilane by reduction with lithium aluminium hydride according to Benkeser, Landesman and Foster¹⁰. The diphenylsilane obtained according to this method distilled at 126–127° (13 mm).

B. Reduction of ethoxy groups with lithium aluminium hydride in dibutyl ether

Tri-n-amylsilane. 28.6 g (0.1 mole) of tri-*n*-amylethoxysilane was introduced dropwise into a stirred slurry of 1.2 g (0.03 mole) of lithium aluminium hydride in 25 ml of dibutyl-ether. It was heated for two hours at 100°. 21 g (87 %) of a substance boiling at 146–153°

(15 mm) was isolated. This product and that prepared without solvent were redistilled together and a fraction was collected at 147° (17 mm) and analysed. (See Table 1.)

Di-n-amylsilane was prepared in the same way from 26.0 g (0.1 mole) of di-*n*-amyl-diethoxysilane and 4.2 g (0.11 mole) of lithium aluminium hydride. The yield was 64 %, boiling at 81–82° (12 mm).

n-Amylsilane. 23.4 g (0.1 mole) of *n*-amyltriethoxysilane and 6.3 g (0.165 mole) of lithium aluminium hydride yielded 3.1 g (30 %) *n*-amylsilane, boiling at 85–87° (748 mm).

n-Amylsilane was also prepared from *n*-amyltrichlorosilane by reduction with lithium aluminium hydride.

n-Amyltrichlorosilane. *n*-Amylmagnesium chloride, prepared from 7.3 g (0.3 g.at.) of magnesium and 32 g (0.3 mole) of *n*-amyl chloride in 100 ml anhydrous ether was added during one hour to 42.5 g (0.25 mole) silicon tetrachloride dissolved in 50 ml ether. Thereafter the reaction mixture was refluxed for two hours. The precipitate of magnesium salts was removed by filtration and washed with ether. Distillation of the filtrate yielded 30.5 g (60 %) *n*-amyltrichlorosilane boiling at 60.5° at 15 mm. Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Baily, Hall, Pietrusza, and Kerr¹¹ obtained a yield of 52 % using amyl bromide, instead of the chloride, and silicon tetrachloride in the molar ratio 1:1.

n-Amylsilane. 27.2 g (0.13 mole) of *n*-amyltrichlorosilane dissolved in 25 ml anhydrous dibutyl ether was added during 30 minutes to a slurry of 4.2 g (0.11 mole) lithium aluminium hydride in 25 ml dibutylether. By direct distillation from the reaction mixture 11.6 g of *n*-amylsilane were collected at 84–86° (760 mm).

C. Preparation with the aid of aluminium chloride

Tri-n-butylsilane. To 12.2 g (0.05 mole) of tri-*n*-butylethoxysilane was added 2.5 g (0.019 mole) of aluminium chloride in one portion. There was a spontaneous slight evolution of heat. The mixture was kept at 80° for a further 10 minutes. After cooling, anhydrous diethyl ether was added whereby a white precipitate was formed (about 2 g). The ether solution was added dropwise to a stirred slurry of 0.6 g (0.016 mole) of lithium aluminium hydride in diethyl ether. After filtration 7.5 g (75 %) of tri-*n*-butylsilane boiling at 104–106° (12 mm) was isolated by distillation.

In an additional experiment equimolecular amounts of tributylethoxysilane and aluminium chloride were used, but the yield (70 %) was not improved. No precipitate was formed when the solution was diluted with ether before reduction.

Di-n-butylsilane. 27.5 g (0.12 mole) of di-*n*-butyldiethoxysilane was stirred in a three-necked flask fitted with reflux condenser, and 12.0 g (0.09 mole) of aluminium chloride was added in portions. The reaction was much more intense than for the trialkyl derivative. After heating for 10 minutes to 80°, 25 ml of ether was added, and the decanted solution introduced dropwise into a slurry of 2.5 g (0.066 mole) of lithium aluminium hydride. 11.8 g (69 %) of di-*n*-butylsilane boiling at 52–53° (15 mm) was isolated.

Di-n-propylsilane was prepared as given above for dibutylsilane from 20.4 g (0.1 mole) of di-*n*-propyldiethoxysilane, 10.6 g (0.08 mole) of aluminium chloride, and 2.2 g (0.06 mole) of lithium aluminium hydride. The yield was 72 %, b.p. 110–111° (1 atm.).

n-Amylsilane. To 12.7 g (0.054 mole) of *n*-amyltriethoxysilane was added in portions 7.0 g (0.052 mole) of aluminium chloride while cooling with water. After dilution with ether reduction was carried out as described above with 1.6 g (0.042 mole) of lithium aluminium hydride. Evolution of small amounts of gas was observed during the reduction. (See below for *n*-hexylsilane.) The yield boiling at 86° (760 mm) was 63 %.

n-Hexylsilane was prepared as just described from 24.8 g (0.10 mole) of *n*-hexyltriethoxysilane, 20.0 g (0.15 mole) of aluminium chloride, and 4.4 g (0.115 mole) of lithium aluminium hydride. The yield was 7.5 g (66 %) of *n*-hexylsilane boiling at 112–113° (761 mm).

The reduction was accompanied by the evolution of a small amount of gas. Part of the gas was collected and ignited. The gas burned giving a white smoke of silicon dioxide. Another sample of gas was absorbed in acetone and tested with 1 % silver nitrate solution. A dark precipitate indicated the presence of reducing groups (Si–H bonds).

Methyl-di-n-propylsilane. *n*-Propylmagnesium chloride was prepared from 4 gram atoms of magnesium in 400 ml of anhydrous ether and 4 moles of *n*-propyl chloride in 200 ml of ether. One mole methyltriethoxysilane in 100 ml of ether was added. After refluxing for

two hours the ether was withdrawn and the reaction mixture was kept at 150° for 12 hours. The ether was again added and the excess of propylmagnesium chloride was decomposed with two moles of anhydrous ethyl alcohol. After filtration and washing with anhydrous ether the filtrate was fractionated. At 126–127° 11 g of methyl-di-*n*-propylsilane was collected. (Found: H 13.8. Calc. for C₇H₁₈Si 13.9). (Furthermore methyl-di-*n*-propyl-ethoxysilane and methyltri-*n*-propylsilane were isolated.)

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