

Infrared Spectra of Alkylsilanes I

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The infrared spectra of 26 alkylsilanes and 2 phenylsilanes have been recorded between 2–15 μ . The wavelength shifts of $\equiv\text{SiH}$, $=\text{SiH}_2$, and $-\text{SiH}_3$ groups in the range 4.6–4.8 μ are reported as well as key bands of alkylsilanes containing $=\text{SiH}_2$, $-\text{SiH}_3$, $=\text{Si}(\text{CH}_3)_2$ and $-\text{Si}(\text{CH}_3)_3$ in the range 10–15 μ .

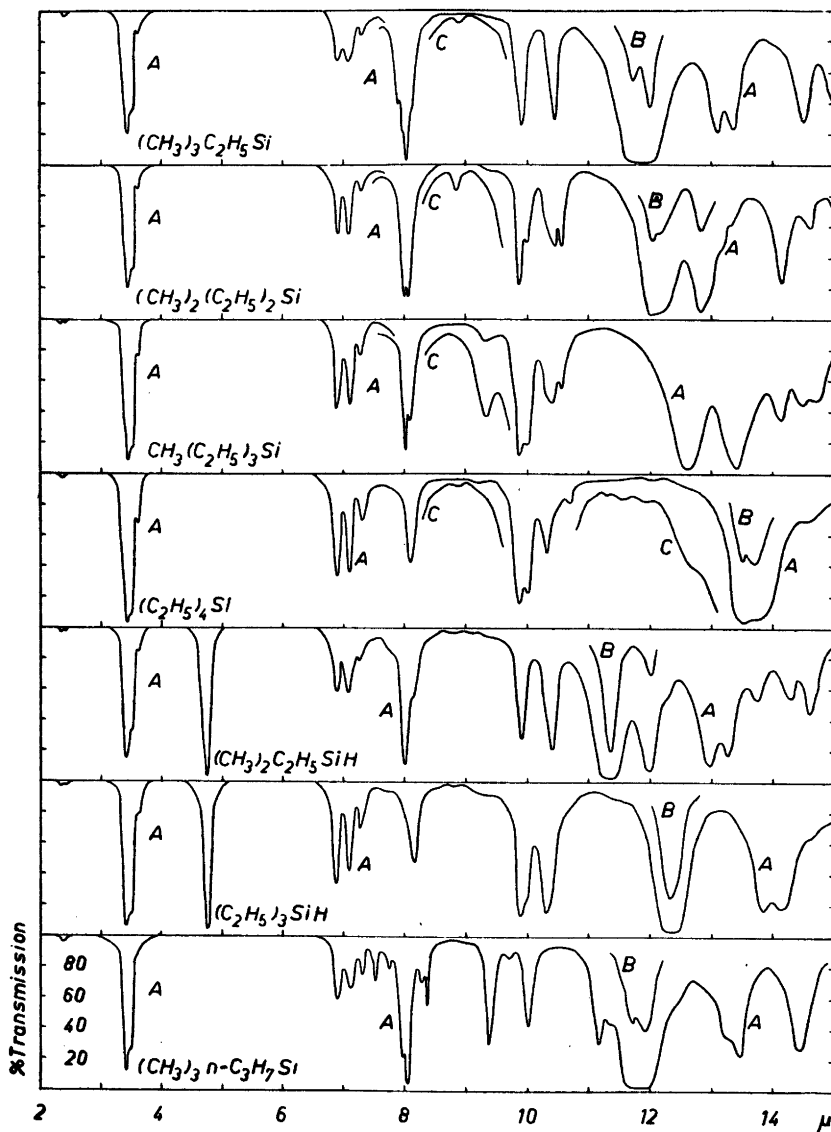
Data on infrared absorption intensities of organic silicon compounds are scarce in the literature. A comparison of spectra of homologues of *n*-alkylsilanes revealed a qualitative relationship between the length of *n*-alkyl-groups and the intensity of some absorption bands. In a subsequent paper numerical data on the intensities of five absorption bands between 6.8 and 8.5 μ will be given.

All the silicon hydrides strongly absorbed at 4.6–4.75 μ . It was found that the absorption wavelength was dependent on the number of hydrogen atoms bonded to the silicon atom in alkylsilanes. Thus all monoalkylsilanes ($-\text{SiH}_3$) absorbed at 4.62 μ , the dialkylsilanes ($=\text{SiH}_2$) at 4.68–4.69 μ and the trialkylsilanes ($\equiv\text{SiH}$) at 4.74 μ . Diphenylsilane absorbed at 4.64 μ and triphenylsilane at 4.68 μ .

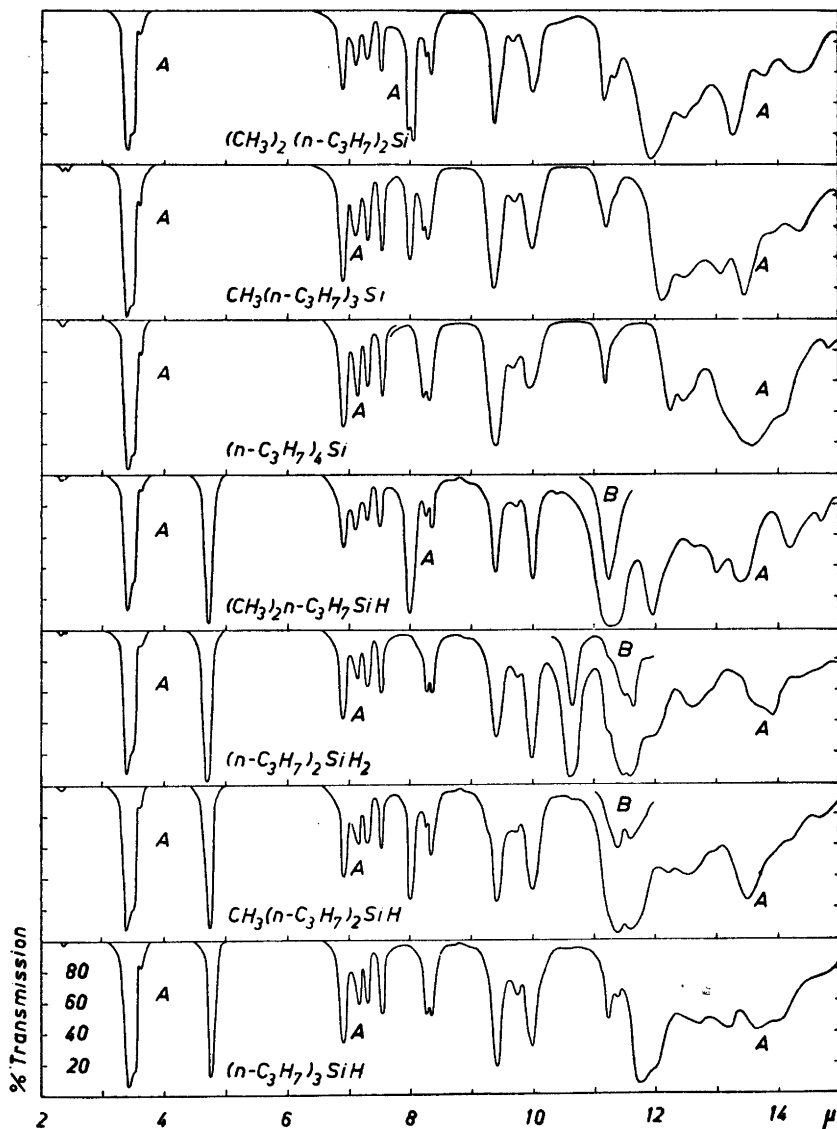
Of the three alkylsilane absorption bands between 6.8 and 7.3 μ (see the figures on pp. 948–951) two are also found in the spectra of paraffins. The C—H bending vibrations in methyl (asymmetric) and methylene groups appear at 6.85–6.86 μ and the symmetric C—H bending vibrations of the methyl groups at 7.27 μ . Near 7.1 μ alkyl silanes give absorption which is not found for corresponding alkanes. Alkylsilanes containing propyl or higher *n*-alkyl groups absorb at about 7.5 μ . For butyl or longer chains there are some weak absorption bands between 7.5–8.0 μ , in which range CH_2 wagging and twisting modes appear in the alkane spectra.

In the range 7.8–8.6 μ the alkylsilanes absorbed in the way described by Kay and Tannenbaum¹ and Harvey *et al*².

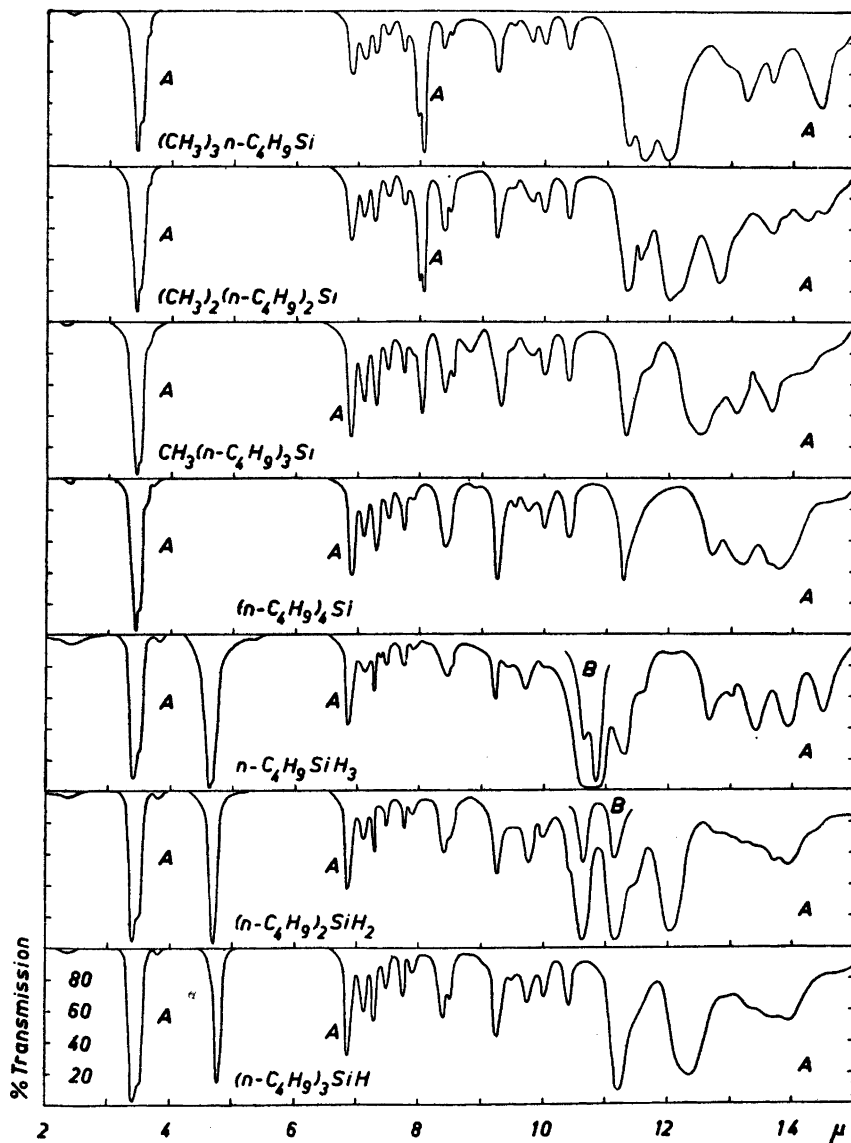
The range 10–15 μ shows absorption bands which are useful for the correlation of chemical structures of alkylsilanes. All the monoalkylsilanes investigated showed strong absorption in 10 % solution in carbon disulfide at 10.6–11.0 μ which on dilution to 1 % solution resolved into two bands at 10.6–



10.7 μ (medium) and 10.85 μ (very strong). The $-\text{SiH}_3$ group gave a characteristic triplet of bands of moderate strength at 13.4–13.5, 14.0 and 14.4–14.5 μ . The dialkylsilanes, *i. e.*, compounds containing the $=\text{SiH}_2$ group, all gave a strong band in 10 % solution, medium in 1 % solution, at 10.6–10.7 μ . However, the very strong band at 10.85 μ for the $-\text{SiH}_3$ group was not found here. Weak absorption at 11.2 μ and 14.0 μ was found in the spectra of all dialkylsilanes, but does not seem to be of great value for the correlations.

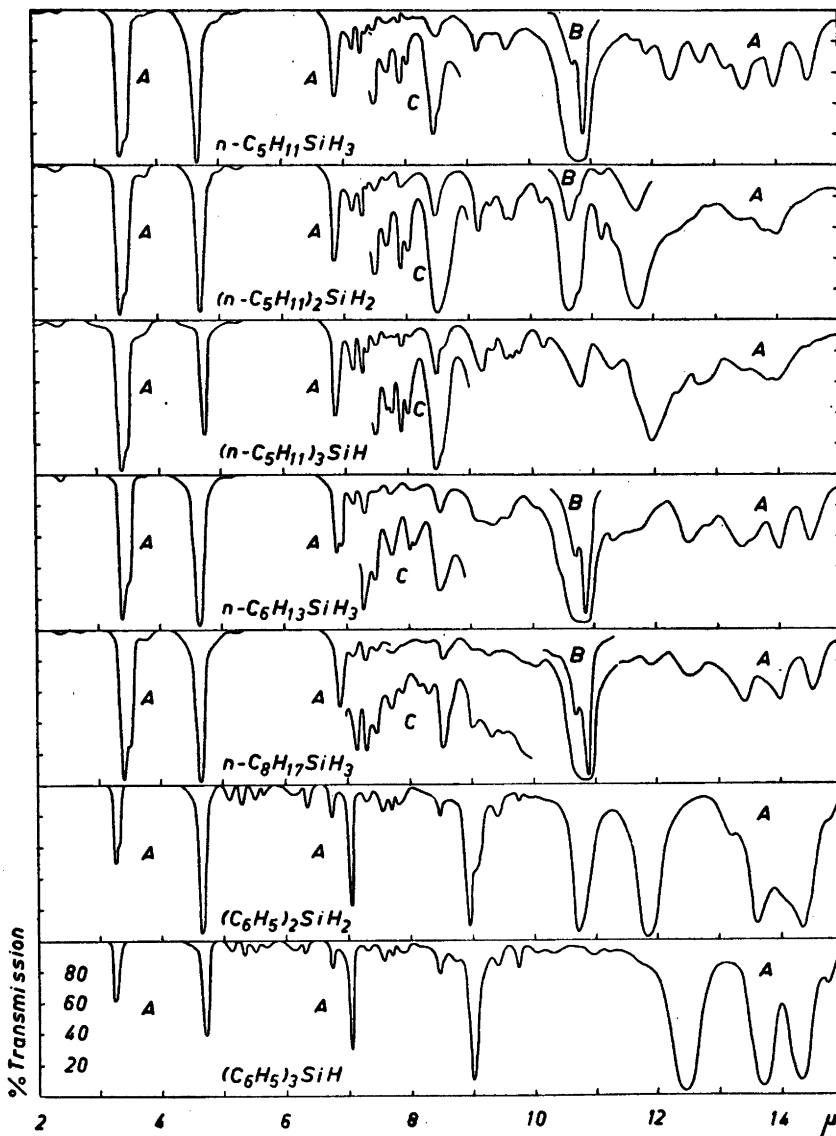


The tetraalkylsilanes containing the trimethylsilyl group showed strong absorption at $11.6\text{--}12.1\ \mu$ in 10 % solutions in carbon disulfide. In 1 % solution the absorption resolved into two bands of about equal strength at $11.6\text{--}11.7\ \mu$ and $12.0\ \mu$. Wright and Hunter³ reported the Si—C stretching mode to appear at $11.63\ \mu$ in tetramethylsilane and at $11.88\ \mu$ in terminal groups —O—Si(CH₃)₃ of linear methylpolysiloxanes. Further the trimethylsilyl group gave a less prominent band at $14.4\text{--}14.5\ \mu$. The alkylsilanes containing



the group $=\text{Si}(\text{CH}_3)_2$ also show strong absorption at 12.0μ in both 10 % and 1 % solutions. This type of compounds can be distinguished from alkyltrimethylsilanes through the absence of the 11.7μ band.

All the bands in the range 10—15 μ described here are, if not otherwise stated, characteristic for the configurations of the investigated substances and should be suitable for identification purposes.



EXPERIMENTAL

The spectra were recorded with a Beckman spectrophotometer model IR-2, equipped with a rock salt prism, and a Brown Electronik pen recorder. Calibration of the wavelength scale was carried out against the values given by Oetjen *et al.*⁴ for CO_2 : 4.225, 14.97 μ and H_2O : 6.903 μ . The cell thickness was 0.10 mm. All spectra were measured in about 10 % solutions in the wave length range 2–15 μ . In some cases spectra of pure substances or of about 1 % solutions were recorded. Carbon tetrachloride was used as the

solvent between 2 and 8 μ and carbon disulfide in the range 7.6–15 μ . In the figures on pp. 948–951 the concentrations are given as follows: A ca. 10 %; B ca. 1 %; C = pure substance.

All molecular refractivities were calculated in the manner previously described⁵. The bond refractivity of the silicon chlorine bond, 7.20, given by Warrick⁶ was used.

Preparative part

The substances containing Si-H bonds were prepared by reduction of alkylethoxysilanes⁵ or of chlorosilanes with lithium aluminium hydride. The chlorosilanes were prepared either from silicon tetrachloride and alkylmagnesium chloride or from disiloxanes according to the methods of Flood⁷ or Voronkov *et al.*⁸

The tetraalkylsilanes were prepared from alkylchlorosilanes and alkylmagnesium chloride or bromide or purified from material available in this laboratory. Dimethyldi-*n*-propylsilane and methyltri-*n*-propylsilane were identical to the samples previously reported⁹. The methyl-*n*-butylsilanes were samples from the work of Larsson and van der Gilse van der Pals¹⁰. The refractive indices of the used samples were remeasured.

Trimethylethylsilane and *trimethyl-*n*-propylsilane* were prepared from trimethylchlorosilane and the appropriate Grignard reagent according to method II of Whitmore *et al.*¹¹. (These authors used another method for the preparation of the substances described here).

The preparation of trimethyl-*n*-propylsilane may be described as an example for both syntheses.

n-Propylmagnesium chloride was prepared from 7.2 g (0.3 g atom) of magnesium, 23.7 g (0.3 mole) of *n*-propyl chloride, and 40 ml of anhydrous ether in a 500 ml apparatus. To the solution was added 11 g (0.1 mole) of trimethylchlorosilane dissolved in 15 ml anhydrous ether during 20 minutes and the reaction mixture was boiled for one hour. After hydrolysis with 5 *N* hydrochloric acid, distillation of the product gave 7.5 g (65 %) of trimethyl-*n*-propylsilane boiling at 88° (1 atm). n_D^{20} 1.3932.

Ethyl bromide was used in the preparation of trimethylethylsilane. The yield was 60 %. B. p. 62°. n_D^{20} 1.3832.

Methyltriethylsilane was prepared from triethylchlorosilane and Grignard reagent according to Whitmore *et al.*¹¹ Methylmagnesium chloride was used instead of the bromide. The yield of methyltriethylsilane was 56 %. B. p. 126–127° (1 atm). n_D^{20} 1.4165.

Dimethylethylchlorosilane was prepared by a Flood reaction. 1,1,3,3-tetramethyl-1,3-diethyl-disiloxane (127 g) was shaken with 100 ml of concentrated sulphuric acid. To the solution was added 75 g of sodium chloride and 75 g of ammonium chloride in portions. The upper layer was collected and distilled, giving 105 g of dimethylethylchlorosilane boiling at 87–92° (1 atm).

Dimethylethylsilane. To a slurry of 8.0 g (0.21 mole) of lithium aluminium hydride in 15 ml of anhydrous dibutyl ether was added 92 g (0.75 mole) of dimethylethylchlorosilane during half an hour. The reaction was spontaneous and accompanied by the evolution of heat. When about half of the chlorosilane had been added, slight external heating was applied and the dimethylethylsilane was removed continuously through a short Vigreux column. The yield of dimethylethylsilane was 63.6 g (95 %) boiling at 44–46°. (Found: Si 32.0. Calc. for C₄H₁₂Si: Si 31.8). d^{20} 0.6679; n_D^{20} 1.3789; MR_D found 30.52, calc. 30.46.

*Dimethyl-*n*-propylchlorosilane* was prepared from 56 g of 1,1,3,3-tetramethyl-1,3-di-*n*-propyl-disiloxane (see below), 40 ml of concentrated sulphuric acid and 40 g of ammonium chloride. Distillation yielded 56 g of dimethyldi-*n*-propylchlorosilane boiling at 113–115°. (Found: Si 20.6 Calc. for C₆H₁₄ClSi: Si 20.5). d^{20} 0.8753; n_D^{20} 1.4133; MR_D found 38.97, calc. 39.20.

*1,1,3,3-tetramethyl-1,3-di-*n*-propyl-disiloxane* was prepared from dimethyl-*n*-propylethoxysilane. (Of course it is more convenient to use the ethoxysilane directly for the preparation of the chloride, without isolating the disiloxane).

To 36 g (0.25 mole) of ice-cooled dimethyl-*n*-propylethoxysilane was added slowly 50 ml of concentrated sulphuric acid. After standing for 14 hours the mixture was poured out on ice. Two layers were formed and separated. The diluted sulphuric acid solution was extracted with ether. The ether solution of all organic material was washed with

water, 25 ml of a 5 % sodium carbonate solution, water again and dried with calcium chloride. Distillation yielded 25.2 g of tetramethyldi-*n*-propyldisiloxane boiling at 66° (11 mm). (Found: Si 26.6. Calc. for C₁₀H₂₆OSi₂: Si 26.5). d^{20} 0.8027; n_D^{20} 1.4098; MR_D found 67.41, calc. 67.46.

Methyldi-*n*-propylchlorosilane was prepared from methyldi-*n*-propylethoxysilane analogous to dimethyl-*n*-propylchlorosilane, but the disiloxane was not isolated. (See below). Methyldi-*n*-propylchlorosilane boiled at 161° (1 atm). (Found: Si 17.0. Calc. for C₁₇H₁₇ClSi: Si 17.0). d^{20} 0.8784; n_D^{20} 1.4300; MR_D found 48.44, calc. 48.46.

1,3-Dimethyl-1,1,3,3-tetra-*n*-propyldisiloxane was prepared from methyldi-*n*-propylethoxysilane in a separate experiment, as described for tetramethyldi-*n*-propyldisiloxane. B. p. 115–116° (12 mm). (Found: Si 20.5. Calc. for C₁₄H₃₄OSi₂: Si 20.5). d^{20} 0.8217; n_D^{20} 1.4290; MR_D found 86.15, calc. 85.99.

The following four alkylsilanes were prepared by reduction of corresponding alkylchlorosilanes with lithium aluminium hydride in diethyl ether:

Silane:	B. p. °C	d^{20}	n_D^{20}	MR _D	
				found	calc.
Dimethyl- <i>n</i> -propyl-	73–74	0.6976	1.3927	34.96	35.21
Methyldi- <i>n</i> -propyl-	127	0.7327	1.4140	44.43	44.48
Triethyl-	107	0.7313	1.4124	39.60	39.40
<i>n</i> -Butyl-	54	0.6772	1.3926	31.07	31.06

n-Octylsilane was also prepared by reduction of the *n*-octyltrichlorosilane by a modified method, where the chlorosilane was never isolated. *n*-Octylmagnesium bromide was prepared from 49 g (0.25 mole) of *n*-octyl bromide and 6.1 g (0.25 g atom) of magnesium in 50 ml of anhydrous ether. The Grignard reagent was filtered and added to a stirred solution of silicon tetrachloride, 43 g (0.25 mole) in 75 ml of ether, during 40 minutes. After rapid filtration through glass wool the solvent and the unreacted silicon tetrachloride were removed by distillation in order to prevent the formation of SiH₄ in the following reduction. Anhydrous ether (ca. 75 ml) was again added and the solution was introduced into a stirred slurry of 9 g (0.25 mole) of lithium aluminium hydride in 50 ml of anhydrous ether.

Direct distillation at 20 mm yielded 19 g (50 %) of *n*-octylsilane boiling at 59–63°. After redistillation the following data were found. B. p. 61° (20 mm). (Found: Si 19.4. Calc. for C₈H₂₀Si: Si 19.5). d^{20} 0.7457; n_D^{20} 1.4253; MR_D found 49.52, calc. 49.61.

The distillation residue was hydrolysed with diluted hydrochloric acid. No di-*n*-octylsilane could be isolated.

Triphenylsilane. Triphenylchlorosilane was prepared by adding phenyllithium (0.31 mole as a 0.94 *N* ether solution) to silicon tetrachloride (0.1 mole) dissolved in ether (100 ml). The precipitate was removed and the ether solution was added to 1.2 g (0.032 mole) of lithium aluminium hydride in ether (100 ml). After completion of the reduction the reaction mixture was rapidly filtered and about 400 ml of ether was distilled off. Excess of lithium aluminium hydride was decomposed by adding the solution to 50 ml of 5 *N* hydrochloric acid. The ether layer was dried with calcium chloride and distilled, yielding 11 g of triphenylsilane, boiling at 148–151° at 1 mm. After one hour the substance solidified. M. p. 35°.

The refractive indices of the following compounds will be given: dimethyldiethylsilane 1.4014, tetraethylsilane 1.4270, tetra-*n*-propylsilane 1.4386, tetra-*n*-butylsilane 1.4468.

I should like to express my appreciation to the director of this institute, Professor Erik Larsson, for his interest in this work.

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Received April 4, 1955.