Alkylchlorosilanes

Two-step process permits control of SiH content of chlorosilanes

 $O_{\text{RGANOSILICON}}$ compounds having both hydrogen and alkyl groups attached to the same silicon atom are obtained in small amounts as by-products of the direct reaction of alkyl chlorides with silicon metal (11). They have been prepared in the laboratory by alkylation of chlorosilanes with Grignard reagents or other metal alkyls (6, 8, 12)

 $2RMgCl + H_2SiCl_2 \rightarrow R_2SiH_2 + 2MgCl_2$ (1)

and by vapor phase reaction of hydrogen with alkylchlorosilanes in the presence of zinc or aluminum (9)

 $\begin{array}{rcl} 6\mathrm{RSiCl}_3 \ + \ 3\mathrm{H}_2 \ + \ 2\mathrm{Al} \ \rightarrow \ 6\mathrm{RSiHCl}_2 \ + \\ & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$

The reaction of alkylchlorosilanes with lithium aluminum hydride in diethyl ether (8)

$$\begin{split} 2R_2 \mathrm{SiCl}_2 + \mathrm{LiAlH}_4 &\rightarrow 2R_2 \mathrm{SiH}_2 + \\ & \mathrm{LiCl} + \mathrm{AlCl}_3 \quad (3) \end{split}$$

is very useful for preparations on a small scale, but the high cost of lithium aluminum hydride makes it unsatisfactory for large quantities. Although previous attempts to use sodium hydride for the conversion of SiCl to SiH (8, 10, 12)were unsuccessful, an investigation of the reaction between chlorosilanes and sodium hydride was undertaken.

The chlorosilane investigated most extensively was methyltrichlorosilane, CH_3SiCl_3 . Preliminary experiments showed that it was converted to methyl-silane when it was passed through a packed bed of granular sodium hydride at 300° C.,

$$CH_3SiCl_3 + 3NaH \rightarrow CH_3SiH_3 + 3NaCl_4$$

Better results were obtained when the chlorosilane vapor was passed through a suspension of finely divided sodium hydride in mineral oil. High conversion could be achieved at 250° C., and this method was used in this work.

Apparatus and Technique

The chlorosilanes were commercially available materials, further purified by fractional distillation.

Reduction of Alkylchlorosilanes by Sodium Hydride and Hydrogen-Chlorine Interchange in Chlorosilanes

ALFRED R. GILBERT, GLENN D. COOPER, and RAY W. SHADE Research Laboratory, General Electric Co., Schenectady, N. Y.

The sodium hydride was purchased (Metal Hydrides, Inc., Beverly, Mass.) as a 22% suspension in mineral oil and reduced to a 15 to 16% suspension at the time of use by addition of mineral oil. The supplier gave the particle size as 5 to 25 microns.

Reactor. The reactor had a 4-inch inside diameter at the top, which reduced to a 2-inch diameter cylinder that constituted the main body. The total height was 13 inches.

Four vertical baffles $(^{3}/_{16}$ inch high) were equally spaced along the inside wall. Agitation was provided by two centrally located flat-bladed turbines (8 blades each, $1^{3}/_{8}$ inch diameter). A constant agitator speed of 1800 r.p.m. was used in all experiments reported. The chlorosilane feed line entered the reactor near the bottom and terminated in a pattern of fine holes directly below the lower turbine.

The reactor was heated by resistance windings on the outside wall and the temperature was controlled by an electric pyrometer control unit. To reduce heat losses, the sides and bottom of the reactor were covered with magnesia lagging and the top with loose diatomaceous earth.

Flow System and Procedure. Prior to each run approximately 475 grams of 15 to 16 weight % sodium hydride was charged to the reactor. While the reactor was being heated, it was swept with dry nitrogen. When the desired temperature was reached, the nitrogen flow was stopped and the chlorosilane flow started. The feed was metered continuously (1 to 2 ml. of liquid per minute) from the reservoir to a vaporizer and then into the reactor. In a few instances the vapor was blended with hydrogen gas before it entered the reactor. The normal feed stream temperature was 120° to 140° C. The vapor leaving the top of the reactor was directed into a 100° C. partial condenser which removed the mineral oil vapor (also any entrained droplets) and returned it to the reactor. After being stripped of mineral oil, the product vapor passed through steam-traced lines to the sampling station.

Sampling Method. The product vapor flowed through the sampling station, was mixed with nitrogen, and exhausted from the system. Periodically a 300-ml. portion of the vapor was isolated in the sample trap and transferred to the evacuated mixing chamber, where it was condensed by means of liquid nitrogen. Following removal of the small amount of noncondensables sometimes present, the product was reexpanded and mixed by magnetically operated paddles sealed in the mixing chamber. A 200-ml. fraction of the vapor then was collected in an evacuated sample bulb for molecular weight determination by the vapor density method.

In several cases, the 200-ml. samples were combined and analyzed by infrared and distillation to assure that no



High conversions to SiH compounds are obtained when chlorosilane vapors are passed through a suspension of sodium hydride in mineral oil



significant side reactions had occurred. In a few runs the total product stream was collected and distilled.

At the end of each run the reactor was drained, and the slurry was analyzed for sodium chloride and sodium hydride.

Results

Product Composition. The major product of the reaction is methylsilane, in which all the chlorines have been replaced by hydrogen; only small amounts of the partially reacted compounds, methylchlorosilane, CH₃SiH₂Cl, and methyldichlorosilane, CH3SiHCl2 are formed (Table I). Methyltrichlorosilane was passed through the reactor until the molecular weight of the product stream was approximately that of pure methyltrichlorosilane. The total product was then analyzed by fractional distillation in a low-temperature Podbielniak column rated at 100 theoretical plates. At 250° C., 93 mole % of the SiH-containing product was methylsilane, the remainder methylchlorosilane (3.2%) and methyldichlorosilane (3.5%). The proportion of the partially reacted materials was somewhat higher at 200°, but methylsilane still accounted for 86%.

| Trichlorosilane | with Sodium | n of Methyl Hydride |
|------------------------------------|------------------|------------------------|
| The product is pr | edominantly m | ethylsilane |
| | \mathbf{M} ole | %ª |
| Component | 200° C. | 250° C. |
| CH_3SiH_3 | 86.0 | 93.3 |
| CH_3SiH_2Cl | 7.6 | 3.2 |
| CH ₃ SiHCl ₂ | 6.4 | 3.5 |

The variation in the product distribution during a run at 250° is shown in Table II. The chlorosilane vapor was diluted with a stream of hydrogen. The product was collected in a liquid nitrogen trap. After approximately 0.2 mole of methyltrichlorosilane had passed through the reactor, the trap was replaced and another fraction was collected. Each fraction was analyzed by fractional distillation. There was a definite trend toward higher proportions of the partially reacted compounds as

Table II. There Is a Trend to Higher Proportions of Partially Reacted Compounds as Sodium Hydride Is Consumed in a Run at 250° C.

| Fraction | % NaH | % Chlorine | Produc | et Composition, | Mole $\%^d$ |
|----------|--------------|------------|-------------|-------------------|---------------|
| No.ª | $Consumed^b$ | Replaced | CH_3SiH_3 | $CH_{3}SiH_{2}Cl$ | CH_3SiHCl_2 |
| 1 | 16.1 | 64.5 | 95.4 | 2.3 | 2.3 |
| 2 | 31.7 | 54.5 | 90.2 | 3.8 | 6.0 |
| 3 | 43.2 | 39.3 | 84.8 | 6.1 | 9.1 |
| 4 | 50.6 | 23.3 | 74.0 | 10.1 | 15.9 |
| 5 | 57.3 | 21.8 | 77.2 | 7.8 | 14.0 |
| 6 | 61.0 | 12.5 | 72.2 | 11.1 | 16.7 |
| 7 | 64.0 | 9.6 | 78.6 | 7.2 | 14.2 |
| 8 | 65.9 | 6.0 | 82.5 | 5.8 | 11.7 |

^a Each corresponds to approximately 0.2 mole CH₃SiCl₃ fed to reactor. ^b% of original NaH charge (2.4 moles) consumed at end of each cut. ^c% of total SiCl fed to reactor during collection of each fraction converted to SiH. ^d Exclusive of unreacted CH₃SiCl₃.

the sodium hydride was consumed, but CH_3SiH_2Cl and CH_3SiHCl_2 combined never exceeded 23% of the total SiH-containing product.

The tendency toward complete replacement of all the chlorine in a molecule probably indicates that the partially reacted products are more reactive toward sodium hydride than the starting material, although it may be due to the fact that once a chlorosilane molecule is adsorbed on the sodium hydride surface it reacts completely before being desorbed. The preponderance of CH₃SiH₃ cannot be due to disproportionation of the intermediate products to methylsilane and methyltrichlorosilane, as CH₃SiHCl₂ is the major product of such a redistribution.

Sodium Hydride Utilization. The change in conversion during a run is shown in Figure 1, in which the composition of the product stream is plotted against the per cent of sodium hydride consumed. The values for the per cent chlorine replaced were calculated from the product molecular weight as determined by vapor density measurements. These values, combined with the knowledge of the amount of methyltrichlorosilane fed to the reactor allowed the calculation of per cent sodium hydride consumed. At 250° C. the extent of reaction was almost 100% initially (exit gas pure CH3SiH3) and decreased very slowly until about 80% of sodium hydride was consumed, then dropped sharply. At 200° the reaction was only about 80% complete at the start, and the conversion decreased rather rapidly as sodium hydride was consumed.

The values for total sodium hydride consumption calculated from the product stream molecular weight agreed within 2% with those determined by analysis of the reactor residues.

Reaction of Other Alkylcholorosilanes. The reaction appears to be generally useful for replacing chlorine by hydrogen in alkylchlorosilanes. At 250° C., trimethylchlorosilane was converted to trimethylsilane, diethyldichlorosilane to diethylsilane, and vinyltrichlorosilane to vinylsilane.

$(CH_3)_3SiCl + NaH \rightarrow (CH_3)_3SiH + NaCl$

$$(C_2H_5)_2SiCl_2 + 2NaH \rightarrow$$

$$(C_2H_5)_2SiH_2 + 2NaCl$$

 $CH_2 = CHSiCl_3 + 3NaH \rightarrow CH_2 = CHSiH_3 + 3NaCl$

HYDROGEN-CHLORINE INTER-CHANGE IN CHLOROSILANES

The principal product of Reaction 5

 $RSiCl_3 + 3NaH \rightarrow RSiH_3 + 3NaCl$ (5)

is the one in which all the chlorines are replaced by hydrogen. Only small amounts of the intermediates, $RSiH_2Cl$ and $RSiHCl_2$, are obtained. Because alkyldichlorosilanes are widely used in silicon technology as precursors to waterrepellent fluids, it is desirable to convert the $RSiH_3$ compounds to the more useful $RSiHCl_2$ structure.

Hydrogen atoms attached to silicon can be replaced by chlorine by reaction with chlorine (16, 17)

 $RSiH_3 + 2Cl_2 \rightarrow RSiHCl_2 + 2HCl$ (6)

or with hydrogen chloride in the presence of aluminum chloride (16).

 $RSiH_3 + 2HCl \rightarrow RSiHCl_2 + 2H_2$ (7)

Both methods utilize available SiH very inefficiently. A more attractive process could be realized by means of a redistribution reaction.

$$RSiH_3 + 2RSiCl_3 \rightarrow 3RSiHCl_2$$
 (8)

The over-all process, combining 5 and 8 would then be

 $RSiCl_3 + NaH \rightarrow RSiHCl_2 + NaCl$ (9)

Groups Attached to Silicon

The redistribution of groups attached to silicon has been extensively studied (5). A few redistributions occur spontaneously, but in most cases a catalyst is required. The aluminum chloridecatalyzed exchange of alkyl or aryl groups with chlorine has been the subject of many investigations (4, 5, 13, 14, 19), but relatively little work has been reported on the exchange of hydrogen with chlorine in alkylchlorosilanes. Whitmore (18) found that triethylsilane and diethyldichlorosilane reacted to give triethylchlorosilane, diethylchlorosilane, and diethylsilane

$$(C_{2}H_{5})_{3}SiH + (C_{2}H_{5})_{2}SiCl_{2} \xrightarrow{Al_{2}Cl_{6}} (C_{2}H_{5})_{3}SiCl + (C_{2}H_{5})_{2}SiHCl + (C_{2}H_{5})_{2}SiHCl + (C_{2}H_{5})_{2}SiH_{2} \quad (10)$$

Disproportionations of the type

$$2\mathrm{RSiHCl}_{2} \xrightarrow{\mathrm{Al}_{2}\mathrm{Cl}_{6}} \mathrm{RSiH}_{2}\mathrm{Cl} + \mathrm{RSiCl}_{3}$$
(11)

were investigated by Dolgov and others (7) and have been obtained by using nitriles (1), dialkylcyanamides (2), and combinations of nitriles or cyanamides with metal halides (3) as catalysts.

Methylsilane with Methyltrichlorosilane

The reaction of greatest interest in this investigation is the redistribution of methylsilane with methyltrichlorosilane to yield methyldichlorosilane

$$CH_{3}SiH_{3} + 2CH_{3}SiCl_{3} \rightarrow 3CH_{3}SiHCl_{2}$$

(12)

Some redistribution occurred when the mixed vapors were passed over sodium chloroaluminate at 200° to 350° C., but a large amount of hydrogen was formed and the recovery of SiH compounds was low. Better results were obtained in liquid phase reactions.

Table III shows the composition of products obtained when methyltrichlorosilane and methylsilane were heated with 5% aluminum chloride at 100° in a ratio of 6 to 1. The exchange of hydrogen and chlorine was rapid. Considerable redistribution occurred in 1 hour, methylsilane constituting only 6% of the recovered Si-H-containing product. There was no evidence in any experiment of methyl-hydrogen or methylchlorine exchanges, although these will presumably also take place with longer reaction times or more vigorous reaction conditions.

Assuming that no methyl shifts occur, the composition of products expected at equilibrium from a random distribution of hydrogen and chlorine is 0.8% methylsilane, 14.2% methylchlorosilane, and 85.0% methyldichlorosilane. Actually, considerably more methyldichlorosilane is formed than is predicted by a random distribution. After 47 hours, the product consisted of 4% methylchlorosilane and 96% methyldichlorosilane.

Equilibrium constants for the system cannot be determined from the data available, but it can be calculated that for the reaction

$$CH_{3}SiH_{2}Cl + CH_{3}SiCl_{3} \rightleftharpoons 2CH_{3}SiHCl_{2}$$
(13)

the equilibrium constant must be greater than 15.

The ratio of methyltrichlorosilane to methylsilane was kept high, to maximize the conversion of SiH to CH_3SiHCl_2 and minimize the possibility of forming silane, which could result from the dis-

Table III.Reaction of Methylsilane with Methyltrichlorosilane at 100° C.ª GaveRapid Exchange of Hydrogen and Chlorine

| Time. | Product Composition, Mole % ^b | | | % SiH |
|-------|--|-------------------|-------------------|-----------|
| Hours | CH_3SiH_3 | $CH_{3}SiH_{2}Cl$ | $\rm CH_3SiHCl_2$ | Recovered |
| 1 | 5.9 | 29.5 | 64.6 | 90 |
| 3 | 1.8 | 17.1 | 81.1 | 87 |
| 17 | | 7.8 | 92.2 | 87 |
| 47 | ••• | 3.8 | 96.2 | 79 |

 a 0.008 mole CH_3SiH_3 and 0.048 mole CH_3SiCl_3 shaken in 13-ml. bomb with 5% Al_2Cl_6. b Composition of SiH-containing product.

proportionation of methylsilane

 $2CH_3SiH_3 \rightarrow (CH_3)_2SiH_2 + SiH_4$ (14)

No silane was detected in any experiment at a ratio of 6 to 1 or 3 to 1. Substantial amounts of silane were formed when the ratio was 2 to 1, and silane was a major product of reactions at a 1 to 1 ratio. Solutions having the 6 to 1 mole ratio can be obtained by saturating methyltrichlorosilane with methylsilane at atmospheric pressure and -20° C., avoiding the necessity for mechanical compression of the methylsilane (15).

A few experiments were carried out on a somewhat larger scale than those of Table III, to obtain a more accurate estimate of product composition. When 0.1 mole of methylsilane and 0.6 mole of methyltrichlorosilane were shaken for 3 hours at 100° with 10% of aluminium chloride, the SiH-containing product consisted of 95% methyldichlorosilane and 5% methylchlorosilane, with only a trace of methylsilane. These products accounted for 92% of the SiH originally added. The hydrogen formed could account for 2% of the SiH, and approximately 3% was present in the still residue.

Effect of Aluminum Chloride Concentration

Experiments carried out at 100° C. using reagent grade aluminum chloride of unknown particle size indicated the rate of the reaction was greatly affected by the amount of aluminum chloride added, although it far exceeded the solubility limit. Reproducibility was not good, however. In experiments at 30° in sealed glass tubes, using aluminum chloride resublimed under vacuum and then ground and sieved under nitrogen (Table IV) reproducibility was excellent

Table IV. Variation of Redistribution. Rate with Catalyst Concentration at 30° C.^a

Rate of reaction increases with increasing surface area

| | Al_2Cl_6 | SiH Recovered as |
|----|------------------------|-----------------------|
| % | Particle size, mesh | $CH_3SiHCl_2, \ \%^b$ |
| 10 | -100 | 46.4 |
| 10 | 60-100 | 36.2 |
| 20 | -100 | 58.5 |

 a 0.008 mole of CH₃SiH₃ and 0.048 mole of CH₃SiCl₃ sealed in glass tubes with Al₂Cl₆ and shaken 5 hours. b % of total SiH added as CH₃SiH₃ recovered as CH₃SiHCl₂.

The rate of redistribution was considerably increased by increase in the amount of catalyst added or decrease in the particle size of catalyst. The solubility of aluminum chloride in methyl-

trichlorosilane is only 0.11% at 30°. When methyltrichlorosilane was shaken at 30° with 10% of aluminum chloride (60 to 100 mesh), the solution was essentially saturated after only 1 hour. As the total reaction time for the experiments in Table IV was 5 hours, the differences in rate of reaction cannot be explained by differences in the rate of solution of the catalyst. Under these conditions the reaction is probably largely heterogeneous, occurring on the aluminum chloride surface.

Other Sources of SiH

Methyldichlorosilane can be produced by redistributing methyltrichlorosilane with many silanes other than methylsilane. The results obtained with a number of silanes at a chlorine-hydrogen ratio of 6 to 1 are listed in Table V. Under the conditions used (5% aluminum chloride; 17 hours at 100°) methylsilane, dimethylsilane, and trimethylsilane were about equally effective; 80% of the SiH was recovered as CH₃-SiHCl₂. Silane was much less effective (18% conversion to CH₃SiHCl₂) and SiHCl₃ gave no detectable reaction, even at 150°.

Although only hydrogen-chlorine shifts were observed in the reactions of methyltrichlorosilane with the methylsilanes, the reaction of dimethyldichlorosilane with dimethylsilane yielded a variety of products, including methylsilane and trimethylchlorosilane, which could have been formed only as a result of shifting of methyl groups.

Ease of Exchange of **Groups Attached to Silicon**

The ease with which a group X attached to silicon exchanges with a group Y on another molecule is greatly affected by the nature of the other groups attached to the silicon atoms-dimethyldichlorosilane redistributes more readily with trimethylchlorosilane than with methyltrichlorosilane (18). Nevertheless, data permit some conclusions as to the relative order of reactivity of different groups in the aluminum chloridecatalyzed redistribution of silicon compounds.

Trimethylsilane, (CH3)3SiH, gave essentially the equilibrium mixture of CH_3SiH_3 , $(CH_3)_2SiH_2$, $(CH_3)_3SiH$, and $(CH_3)_4Si$ when shaken at 30° for 5 hours with 10% of aluminum chloride; trimethylethylsilane showed no detectable reaction. Tetramethylsilane did not redistribute with methyltrichlorosilane under these conditions although extensive hydrogen-chlorine redistribution took place between methylsilane and methyltrichlorosilane (Table IV). These observations indicate that hydrogen-chlorine or hydrogen-alkyl shifts occur much more readily than alkyl-alkyl or alkyl-chlorine

shifts. These results, with Whitmore's report that only hydrogen-chlorine shifts took place in the redistribution of triethylsilane with diethyldichlorosilane (19), indicate that hydrogen-chlorine exchanges occur more readily than hydrogen-alkyl exchanges. The relative order of reactivity is, therefore, H-Cl > H-alkyl \gg alkyl-alkyl, alkyl-Cl.

| Table | ۷. | Redistributi | ion o | f | CH ₃ SiCl ₃ |
|-------|----|--------------|-------|----|-----------------------------------|
| | wi | th SiH Com | pound | sa | |

| - | | | |
|---|----|-------|--|
| | CU | C:TTC | |

| SiH Source | % ^b |
|-------------------------------------|----------------|
| (CH ₂) ₂ SiH | 83 |
| $(CH_3)_2SiH_2$ | 78 |
| CH ₃ SiH ₃ | 82 |
| SiH_4 | 18 |
| SiHCl ₃ ° | 0 |
| | |

^a 17 hours at 100° C., using 0.048 mole of CH₂SiCl₃, 5% Al₂Cl₆, and a H:Cl ratio of 1:6. b% of SiH initially added recovered as CH_3SiHCl_2 . \circ 150° C.

Experimental

The methylchlorosilanes used were redistilled commercial products. The methylsilanes were prepared by reaction of the methylchlorosilanes with sodium hydride and were redistilled in a Podbielniak low-temperature column. The aluminum chloride was reagent grade material. For some experiments, the aluminum chloride was resublimed under vacuum and then pulverized and sieved under nitrogen in a dry box.

Most of the experiments were carried out in 13-ml. stainless steel bombs. The bomb was loaded in a dry box with chlorosilane and aluminum chloride, sealed, attached to a vacuum train, cooled with liquid nitrogen, and evacuated. The methylsilane was condensed in the bomb, which was then sealed and shaken in a constant-temperature bath. The products were analyzed by distillation in a low-temperature Podbielniak column. Some experiments (Table IV) were carried out in sealed glass tubes. Air was removed from the reactants by repeated freezing and thawing, although small amounts of air had no detectable effect on the reaction. The larger-scale experiments were carried out in 100-ml. stainless steel bombs heated in a rocking autoclave.

Handling of Methylsilane

Methylsilane, unlike silane, is not spontaneously flammable in air, but mixtures of oxygen and methylsilane react explosively in the presence of mercury vapor (16). No difficulty was encountered in handling rather large amounts of methylsilane, repeatedly exposed to air without effect, but an explosion occurred when air was accidentally admitted to a vacuum system

containing methylsilane and mercury vapor.

Conclusions

The reaction of alkylchlorosilanes with sodium hydride at 250° C. is an excellent method for conversion of SiCl to SiH. At least 90% of the sodium hydride is utilized. All the chlorine atoms in an alkylpolychlorosilane molecule tend to be replaced by hydrogen, even when the total extent of reaction is small. Under most conditions, more than 90% of the product from methyltrichlorosilane was methylsilane.

The aluminum chloride-catalyzed redistribution of methyltrichlorosilane with methylsilanes gives good yields of methyldichlorosilane under moderate conditions. Methylsilane, dimethylsilane, or trimethylsilane may be used as sources of SiH. The reaction appears to occur principally on the catalyst surface. The ease of exchange of groups attached to silicon is H-Cl > H-alkyl \gg alkylalkyl, alkyl-Cl.

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