# The synthesis of chlorosilanes from alkoxysilanes, silanols, and hydrosilanes with bulky substituents

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## Abstract

We have found that commercially important trialkylchlorosilanes can readily be synthesized by the reaction of alkoxysilanes, silanols, and hydrosilanes with aqueous concentrated hydorochloric acid. Treatment of trialkylalkoxysilanes bearing the bulky alkyl substituents, such as the *i*-Pr, *sec*-Bu, *tert*-Bu, and *cyclo*-Hex group, with 35% aqueous hydrochloric acid afforded the corresponding trialkylchlorosilanes in excellent yields. Similar treatment of trialkylsilanols with 35% aqueous hydrochloric acid also gave trialkylchlorosilanes in almost quantitative yields. The reaction of methyltrichlorosilane and dimethyldichlorosilane with alkyl-Grignard reagents bearing a bulky alkyl group, followed by treatment of the resulting mixtures with aqueous concentrated hydrochloric acid, produced the respective dialkylmethyl- and alkyldimethylchlorosilanes in high yields. Treatment of trialkylhydrosilanes with concentrated hydrochloric acid in the presence of a palladium catalyst afforded trialkylchlorosilanes in high yields.
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## 1. Introduction

Trialkylchlorosilanes bearing the bulky alkyl substituents, such as *i*-Pr and *tert*-Bu group, are important compounds in the synthetic chemistry as a protecting group for active hydrogen (HO– and HN–), in both scientific and industrial fields. These compounds are also useful materials in the paint industries, and now synthesized commercially by the reaction of trichlorosilane or tetrachlorosilane with Grignard reagents in fairly large quantities.

We have recently found that the reaction of alkoxytrichlorosilanes with various Grignard reagents having a bulky alkyl group produces trialkylalkoxysilanes in high yields [1]. To date, many methods for the conversion of trialkylalkoxysilanes into trialkylchlorosilanes have been reported. In these methods, acylchloride [2], thionyl chloride [3], phosphorus pentachloride [4], phosphorus trichloride [5], tetrachlorosilane [6], and also hydrogen chloride gas [6,7] have been used as chlorinating agents. However, no suitable method for the industrial synthesis of the chlorosilanes from the alkoxysilanes is available so far. More recently, we have discovered that hydrolysis of the mixture obtained from the reaction of *i*-PrMgCl with MeOH, followed by treatment with methyltrichlorosilane, with aqueous concentrated hydrochloric acid affords *i*-Pr$_2$MeSiCl in high yield. We thought that the formation of *i*-Pr$_2$MeSiCl in this reaction comes from the reaction of *i*-Pr$_2$MeSiOMe with aqueous concentrated hydrochloric acid.

On the basis of this finding, we have investigated the reaction of various trialkylalkoxysilanes with concentrated hydrochloric acid to establish the synthetic procedure of trialkylchlorosilanes from trialkylalkoxysilanes. We have also examined to extend this method to trialkylsilanols and trialkylhydrosilanes.

## 2. Results and discussion

### 2.1. Chlorination of trialkylalkoxysilanes

First, we examined the reactions of three tri-isopropylalkoxy-silanes having a MeO, *n*-BuO, and *i*-PrO group as the alkoxy moiety, with a large excess of aqueous concentrated hydrochloric acid. In all cases, *i*-Pr$_3$SiCl was obtained in excellent yields. The optimum conditions concerning the formation of *i*-Pr$_3$SiCl from the alkoxysilanes, however, varied with the sort of the alkoxy group as shown in Table 1.

When 1 equiv. of *i*-Pr$_3$SiOMe was treated with 3 equiv. of 35% aqueous hydrochloric acid (35% aqueous HCl) in the absence of the solvent at room temperature for 2 h, *i*-Pr$_3$SiCl was obtained in 98% yield, after distillation of the organic layer as shown in Scheme 1 (run 1). Similar reaction of *i*-Pr$_3$SiOH with a small excess of 35% aqueous HCl afforded the chlorosilane in 60% yield, in addition to a 40% yield of *i*-Pr$_3$SiOH. In the reaction of *i*-Pr$_3$SiOMe with dilute hydrochloric acid, no *i*-Pr$_3$SiCl was produced. For example, the reaction of 1 equiv. of *i*-Pr$_3$SiOMe with 0.2 equiv. of 5% aqueous hydrochloric acid at 65 °C in THF for 4 h produced a hydrolysis product, *i*-Pr$_3$SiOH in quantitative yield. It is well-known that hydrolysis of trialkyl-chlorosilanes with the bulky substituents gives trialkylsilanols, but not hexaalkyldisiloxanes. In the similar reaction of *i*-Pr$_3$SiOR, which has a bulkier alkoxy substituent than methoxy group, with concentrated hydrochloric acid, the use of THF as a solvent resulted in the higher yield of the product than in the absence of the solvent. In fact, treatment of *i*-Pr$_3$SiOBu-*n* with 4.8 equiv. of 35% aqueous HCl in THF at room temperature produced *i*-Pr$_3$SiCl in 95% yield (run 2). On the other hand, in the reaction of the alkoxysilane with the *sec*-alkoxy group with

$$R_3SiOR' + conc.\ HCl \longrightarrow R_3SiCl$$

R = *i*-Pr, *sec*-Bu, *cyclo*-Hex     R = *i*-Pr, *sec*-Bu, *cyclo*-Hex
R' = Me, *i*-Pr, *n*-Bu

$$i\text{-}Pr_3SiOMe + dil.\ HCl \longrightarrow i\text{-}Pr_3SiOH$$
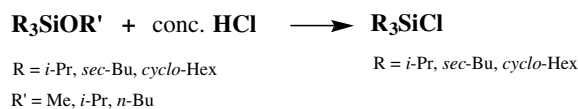
Scheme 1.

35% aqueous HCl, the rate of the chlorination is quite slow, therefore, heating of the reaction mixture is required for obtaining *i*-Pr$_3$SiCl in high yield. Thus, the reaction of 1 equiv. of *i*-Pr$_3$SiOPr-*i* with 4.8 equiv. of 35% aqueous HCl at room temperature for 4 h afforded a trace of *i*-Pr$_3$SiCl, while at 50 °C for 4 h, *i*-Pr$_3$SiCl was produced in 98% yield (run 3).

When trialkylchlorosilanes bearing the bulky substituents, for example, *i*-Pr$_3$SiCl and *i*-Pr$_2$MeSiCl were stirred in 35% aqueous HCl at room temperature, no change was observed. The starting chlorosilanes were recovered quantitatively. However, the reaction of less hindered trialkylchlorosilanes with the hydrochloric acid under the same conditions undergoes hydrolysis to give siloxanes. Indeed, treatment of Me$_3$SiCl with 35% aqueous HCl at room temperature afforded hexamethyldisiloxane in almost quantitative yield.

Tri(*sec*-butyl)alkoxysilanes and tri(cyclohexyl)alkoxysilanes can also be converted into the respective chlorosilanes by the reaction with 35% aqueous HCl in THF in high yields. Thus, treatment of *sec*-Bu$_3$SiOMe and *sec*-Bu$_3$SiO-Bu-*n* with a large excess of 35% aqueous HCl in THF at room temperature gave *sec*-Bu$_3$SiCl in 98% and 97% yields, respectively (run 4,5). Similar reaction of *cyclo*-Hex$_3$SiOMe and *cyclo*-Hex$_3$SiOBu-*n* with 35% aqueous HCl in THF at room temperature afforded *cyclo*-Hex$_3$SiCl in almost quantitative yields (run 6,7).

Table 1
Chlorination of alkoxysilanes with 35%-hydrochloric acid

| Run | Alkoxysilane (mmol) | | HCl (mmol) | Temperature (°C) | Time (h) | Chlorosilane (yield[a] %) | |
|---|---|---|---|---|---|---|---|
| 1 | *i*-Pr$_3$SiOMe | 100 | 300 | 24 | 2 | *i*-Pr$_3$SiCl | 98 |
| 2 | *i*-Pr$_3$SiOBu−*n* | 15 | 72 | 24 | 4 | *i*-Pr$_3$SiCl | 95 |
| 3 | *i*-Pr$_3$SiOPr−*i* | 10 | 48 | 50 | 4 | *i*-Pr$_3$SiCl | 98 |
| 4 | *sec*-Bu$_3$SiOMe | 5 | 36 | 24 | 4 | *sec*-Bu$_3$SiCl | 98 |
| 5 | *sec*-Bu$_3$SiOBu−*n* | 100 | 720 | 24 | 4 | *sec*-Bu$_3$SiCl | 97 |
| 6 | *cyclo*-Hex$_3$SiOMe | 50 | 360 | 24 | 4 | *cyclo*-Hex$_3$SiCl | 99 |
| 7 | *cyclo*-Hex$_3$SiOBu−*n* | 5 | 36 | 24 | 4 | *cyclo*-Hex$_3$SiCl | 98 |
| 8 | *i*-Pr$_2$MeSiOMe | 100 | 480 | 0 | 2 | *i*-Pr$_2$MeSiCl | 99 |
| 9 | *sec*-Bu$_2$MeSiOMe | 100 | 480 | 0 | 2 | *sec*-Bu$_2$MeSiCl | 99 |
| 10 | *cyclo*-Hex$_2$MeSiOMe | 50 | 240 | 0 | 2 | *cyclo*-Hex$_2$MeSiCl | 99 |
| 11 | *i*-PrMe$_2$SiOMe | 10 | 240 | 0 | 1 | *i*-PrMe$_2$SiCl | 97 |
| 12 | *sec*-BuMe$_2$SiOMe | 10 | 240 | 0 | 1 | *sec*-BuMe$_2$SiCl | 99 |
| 13 | *cyclo*-HexMe$_2$SiOMe | 10 | 240 | 0 | 1 | *cyclo*-HexMe$_2$SiCl | 97 |
| 14 | *tert*-BuMe$_2$SiOMe | 50 | 450 | 0 | 2 | *tert*-BuMe$_2$SiCl | 99 |
| 15 | Et$_3$SiOMe | 50 | 450 | 0 | 2 | Et$_3$SiCl | 98 |
| 16 | *i*-PrMe$_2$SiOMe | 50 | Gas[b] | 6–27 | 15 min | *i*-PrMe$_2$SiCl | 99 |
| 17 | *sec*-BuMe$_2$SiOMe | 50 | Gas[b] | 5–18 | 25 min | *sec*-BuMe$_2$SiCl | 99 |
| 18 | *cyclo*-HexMe$_2$SiOMe | 50 | Gas[b] | 5–11 | 50 min | *cyclo*-HexMe$_2$SiCl | 99 |

[a] Yield was determined by GLC.
[b] Hydrogen chloride gas.

## 2.2. Chlorination of dialkylmethyl- and alkyldimethylalkoxysilane

As mentioned above, trialkylalkoxysilanes bearing the less hindered alkyl groups on the silicon atom, such as $R_2MeSiOR'$ and $RMe_2SiOR'$, are rather sensitive toward hydrolysis. In an effort to prevent the hydrolysis of the resulting chlorosilanes, we found that the reaction of the less hindered alkoxysilanes with hydrochloric acid at low temperature, in the presence or absence of the hydrocarbon solvent, produced chlorosilanes in high yields. Interestingly, the use of THF as the solvent in these reactions gave silanols and disiloxanes as the by-products.

Treatment of $i$-$Pr_2MeSiOMe$ with 35% aqueous HCl in the absence of the solvent at 0 °C produced $i$-$Pr_2MeSiCl$ in 99% yield (run 8). Similarly, treatment of $sec$-$Bu_2MeSiOMe$ and $cyclo$-$Hex_2MeSiOMe$ with the hydrochloric acid under the same conditions afforded the respective chlorosilanes in almost quantitative yields (run 9,10). In both reactions, neither silanols nor disiloxanes were detected in the reaction mixtures. The reaction of alkyldimethylmethoxysilanes with concentrated hydrochloric acid also gave alkyldimethylchlorosilane in high yields. Thus, treatment of $i$-$PrMe_2SiOMe$, $sec$-$BuMe_2SiOMe$, $cyclo$-$HexMe_2SiOMe$, and $tert$-$BuMe_2SiOMe$ with 35% aqueous HCl in hydrocarbon at 0 °C produced the respective chlorosilanes in quantitative yields, as shown in Table 1 (run 11–14). The structures of all chlorosilanes obtained in the present reactions were confirmed by mass and $^1H$, $^{13}C$, and $^{29}Si$ NMR spectrometric analysis, and spectral data for known compounds were identical with those of the authentic samples.

## 2.3. Grignard coupling, followed by treatment with 35% aqueous HCl

We found that treatment of the mixture obtained by the reaction of 1 equiv. of methyltrichlorosilane with 4 equiv. of $i$-$PrMgCl$ in THF–toluene, with 35% aqueous HCl at 0 °C gave $i$-$Pr_2MeSiCl$ in 73% yield (run 19) as shown in Table 2. However, for the synthesis of alkyldimethylchlorosilanes, the substitution of the solvent THF to the high boiling hydrocarbon such as toluene and xylene is required to prevent the formation of the hydrolysis product such as silanols. For example, to the mixture formed by the reaction of dimethyldichlorosilane with $i$-$PrMgCl$ in THF was added xylene, and then THF was distilled off from the mixture. Finally, treatment of the resulting mixture with concentrated hydrochloric acid produced $i$-$PrMe_2SiCl$
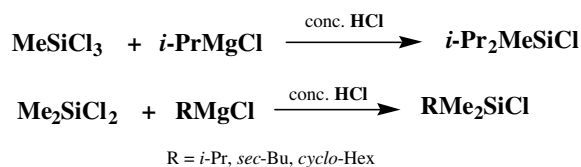
in 80% yield (run 20). Similar treatment of the mixtures produced from the reaction of dimethyldichlorosilane with $sec$-$BuMgCl$ and $cyclo$-$HexMgCl$, with the hydrochloric acid afforded $sec$-$BuMe_2SiCl$ and $cyclo$-$HexMe_2SiCl$ in 79% and 74% yields, respectively (run 21,22) (Scheme 2). In these reactions, no hydrolysis products, silanols and disiloxanes were detected in the reaction mixtures.

In general, the reaction of polychlorosilanes with Grignard reagents giving trisubstituted chlorosilanes always results in the formation of a large amount of magnesium salts, and the magnesium salts thus formed must be removed by filtration to isolate the resulting chlorosilanes. The present method using concentrated hydrochloric acid, however, offers a simple way to obtain the trisubstituted chlorosilanes, because the magnesium salts in the reaction mixtures are able to dissolve completely in concentrated hydrochloric acid. Therefore, after separation of the organic layer from the aqueous layer, the chlorosilanes can readily be isolated by distillation of the organic layer.

## 2.4. Chlorination of trialkylsilanols

Treatment of the Grignard coupling product with concentrated hydrochloric acid probably gives the equilibrium mixture consisting of trialkylchlorosilane and trialkylsilanol. In the case of trialkylchlorosilane bearing a bulky alkyl group, the equilibrium lies far to the formation of the chlorosilane. Furthermore, in the use of a large excess of concentrated hydrochloric acid, the equilibrium increasingly shifts to direction of the chlorosilane as observed in the present reactions. In fact, treatment of $Et_3SiOH$ with 35% aqueous HCl in hexane at 0 °C gave $Et_3SiCl$ in 96% yield (run 23) [8]. Similar reaction of $i$-$Pr_3SiOH$ with concentrated hydrochloric acid at room temperature produced $i$-$Pr_3SiCl$ in quantitative yield (run 24).

We have demonstrated that this reaction can also be used for conversion of alkyldimethylsilanol into the corresponding chlorosilane. Thus, the reaction of $tert$-$BuMe_2SiOH$ with 35% aqueous HCl in hexane at 0 °C afforded

$$MeSiCl_3 \ + \ i\text{-}PrMgCl \xrightarrow{\text{conc. HCl}} i\text{-}Pr_2MeSiCl$$

$$Me_2SiCl_2 \ + \ RMgCl \xrightarrow{\text{conc. HCl}} RMe_2SiCl$$

R = $i$-Pr, $sec$-Bu, $cyclo$-Hex

Scheme 2.

Table 2
Alkylation of $Me_2SiCl_2$ and chlorination with 35%-hydrochloric acid

| Run | Material (mmol) | | Grignard reagent (mmol) | | HCl (mmol) | Product (yield[a] %) | |
|-----|-----------------|-----|-------------------------|-----|------------|----------------------|-----|
| 19 | $MeSiCl_3$ | 120 | $i$-$PrMgCl$ | 480 | 580 | $i$-$Pr_2MeSiCl$ | 73 |
| 20 | $Me_2SiCl_2$ | 48 | $i$-$PrMgCl$ | 71 | 1150 | $i$-$PrMe_2SiCl$ | 80 |
| 21 | $Me_2SiCl_2$ | 43 | $sec$-$BuMgCl$ | 127 | 1030 | $sec$-$BuMe_2SiCl$ | 79 |
| 22 | $Me_2SiCl_2$ | 41 | $cyclo$-$HexMgCl$ | 119 | 980 | $cyclo$-$HexMe_2SiCl$ | 74 |

[a] Yield was determined by GLC.

*tert*-BuMe$_2$SiCl in high yield (run 25), as shown in Table 3. It has been reported that the reaction of *tert*-BuMe$_2$SiOH with thionyl chloride [9] or hydrogen chloride gas [10] yields *tert*-BuMe$_2$SiCl. The reaction of *tert*-BuPh$_2$SiOH with concentrated hydrochloric acid in THF, however, afforded no *tert*-BuPh$_2$SiCl, and recovered *tert*-BuPh$_2$-SiOH in quantitative yield (run 26) [11]. Presumably, introduction of the phenyl groups onto the silicon atom contributes to suppress the nucleophilic attack of Cl$^-$ to this silicon atom.

## 2.5. Chlorination of trialkylhydrosilanes

It has been reported that the reaction of trialkylhydrosilane with hydrogen chloride gas in the presence of a catalyst such as platinum dichloride [12] and Lewis acid [13] affords trialkylchlorosilane. However, no report concerning the reaction of trialkylhydrosilane with aqueous hydrochloric acid so far. We have examined the reaction of trialkylhydrosilane with aqueous concentrated hydrochloric acid, and found that the reaction of the hydrosilane with aqueous concentrated hydrochloric acid in the presence of a catalytic amount of PdCl$_2$ or Pd/C produces trialkylchlorosilane in high yield.

The reaction of *i*-Pr$_3$SiH with 35% aqueous HCl in the presence of 1 mol% of PdCl$_2$ at room temperature for 3 h, *i*-Pr$_3$SiCl was obtained in high yield (run 27), as shown in Table 4. The use of a Pd/C catalyst also led to the similar result (run 28). Interestingly, the Pd/C catalyst can be recovered by filtration of the reaction mixture and reused in the reaction. Et$_3$SiH and *tert*-BuMe$_2$SiH also react with 35% aqueous HCl in the presence of a catalytic amount of PdCl$_2$ or Pd/C to give the respective chlorosilanes. For examples, the reaction of Et$_3$SiH with 35% aqueous HCl in the presence of a PdCl$_2$ catalyst gave Et$_3$SiCl in 97% yield (run 29), while the reaction of *tert*-BuMe$_2$SiH under the same conditions afforded *tert*-BuMe$_2$SiCl in 93% yield (run 30).

In conclusion, the reaction of trialkyl substituted alkoxysilanes and silanols with 35% aqueous HCl gave the respective trialkylchlorosilanes in high yields. Trialkylchlorosilanes were also obtained by the palladium-catalyzed reaction of trialkylhydrosilanes with aqueous concentrated hydrochloric acid in high yields. Treatment of the mixture obtained by the reaction of methyltrichlorosilane and dimethyldichlorosilane with Grignard reagents that have a bulky alkyl group, with aqueous concentrated hydrochloric acid directly afforded the dialkylmethyl- and alkyldimethylchlorosilane in high yields.

## 3. Experimental section

### 3.1. General procedure

All reactions were carried out under an atmosphere of dry nitrogen. NMR spectra were recorded on a JEOL JNM-LA 300 spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. Mass spectra were measured on a JEOL JMS-Automass SUN 200 instrument. Yields of the products were determined by analytical GLC with the use of hydrocarbon such as decane and tridecane as an internal standard.

### 3.2. Chlorination of alkoxytrialkylsilanes by 35% aqueous hydrochloric acid

#### 3.2.1. i-Pr$_3$SiOMe (run 1)

In a 100-ml four-necked flask fitted with a mechanical stirrer, condenser, and thermometer were placed 18.8 g (0.10 mol) of *i*-Pr$_3$SiOMe and 31.3 g (0.30 mol) of 35% aqueous HCl. The mixture was stirred at room temperature for 2 h. The organic layer was separated and analyzed by GLC technique using tridecane as an internal standard as being *i*-Pr$_3$SiCl (98% yield). The organic layer was distilled under reduced pressure to give 18.7 g (98% yield) of *i*-Pr$_3$SiCl (b.p. 78–80 °C/10 Torr). All spectral data obtained

Table 3
Chlorination of silanols with 35%-hydrochloric acid

| Run | Silanol (mmol) | | HCl (mmol) | Temperature (°C) | Time (h) | Chlorosilane (yield[a] %) | |
|-----|----------------|-----|-----------|------------------|----------|----------------------------|-----|
| 23 | Et$_3$SiOH | 10 | 90 | 0 | 2 | Et$_3$SiCl | 96 |
| 24 | *i*-Pr$_3$SiOH | 50 | 150 | 24 | 2 | *i*-Pr$_3$SiCl | 99 |
| 25 | *tert*-BuMe$_2$SiOH | 10 | 90 | 0 | 2 | *tert*-BuMe$_2$SiCl | 98 |
| 26 | *tert*-BuPh$_2$SiOH | 10 | 30 | 40 | 2 | *tert*-BuPh$_2$SiCl | 0 |

[a] Yield was determined by GLC.

Table 4
Palladium catalyzed chlorination of hydrosilanes with 35%-hydrochloric acid

| Run | Hydrosilane (mmol) | | Catalyst (mol%) | | HCl (mmol) | Temperature (°C) | Time (h) | Chlorosilane (yield[a] %) | |
|-----|--------------------|-----|------------------|-----|-----------|------------------|----------|----------------------------|-----|
| 27 | *i*-Pr$_3$SiH | 50 | PdCl$_2$ | 1.0 | 150 | 25 | 3 | *i*-Pr$_3$SiCl | 95 |
| 28 | *i*-Pr$_3$SiH | 50 | Pd/C | 1.0 | 150 | 25 | 3 | *i*-Pr$_3$SiCl | 99 |
| 29 | Et$_3$SiH | 50 | PdCl$_2$ | 1.0 | 1200 | 0 | 2 | Et$_3$SiCl | 97 |
| 30 | *tert*-BuMe$_2$SiH | 50 | PdCl$_2$ | 0.5 | 150 | 25 | 2 | *tert*-BuMe$_2$SiCl | 93 |
| 31 | *tert*-BuMe$_2$SiH | 50 | Pd/C | 0.5 | 150 | 25 | 2 | *tert*-BuMe$_2$SiCl | 97 |

[a] Yield was determined by GLC.

for $i$-Pr$_3$SiCl are identical with those of the authentic sample reported previously [14].

### 3.2.2. i-Pr$_3$SiOBu-n (run 2)

A mixture of 3.46 g (15 mmol) of $i$-Pr$_3$SiOBu-$n$, 7.5 g (72 mmol) of 35% aqueous HCl, and 19 ml of THF was stirred at room temperature for 4 h. The organic layer was separated and analyzed by GLC technique using tridecane as an internal standard as being $i$-Pr$_3$SiCl (95% yield).

### 3.2.3. i-Pr$_3$SiOPr-i (run 3)

A mixture of 2.16 g (10 mmol) of $i$-Pr$_3$SiOPr-$i$, 5.0 g (48 mmol) of 35% aqueous HCl, and 2.5 ml of THF was stirred at 50 °C for 4 h. The organic layer was separated and analyzed by GLC technique using tridecane as an internal standard as being $i$-Pr$_3$SiCl (98% yield).

### 3.2.4. sec-Bu$_3$SiOMe (run 4)

A mixture of 1.15 g (5.0 mmol) of $sec$-Bu$_3$SiOMe, 3.8 g (36 mmol) of 35% aqueous HCl, and 6.5 ml of THF was stirred at room temperature for 4 h. The organic layer was separated and analyzed by GLC technique using tridecane as an internal standard as being $sec$-Bu$_3$SiCl (98% yield).

### 3.2.5. sec-Bu$_3$SiOBu-n (run 5)

A mixture of 27.3 g (0.10 mol) of $sec$-Bu$_3$SiOBu-$n$, 75.0 g (0.72 mol) of 35% aqueous HCl, and 150 ml of THF was stirred at room temperature for 4 h. The organic layer was separated and analyzed by GLC technique using tridecane as an internal standard as being $sec$-Bu$_3$SiCl (97% yield). The organic layer was distilled under reduced pressure to give 20.3 g (86% yield) of $sec$-Bu$_3$SiCl: b.p. 92–93 °C/5 Torr; MS $m/z$ 234 (M)$^+$; $^1$H NMR $\delta$ (CDCl$_3$) 0.95–1.08 (m, 3H, HC–Si), 0.97 (t, 9H, H$_3$C–C–Si, $J = 7.3$ Hz), 1.07 (d, 9H, H$_3$C–C–C, $J = 6.2$ Hz), 1.17–1.31, (m, 3H, –CH$_2$–), 1.65–1.78, (m, 3H, –CH$_2$–); $^{13}$C NMR $\delta$ (CDCl$_3$) 13.4 (CH$_3$), 13.5 (CH$_3$), 21.3 (CH–Si), 24.3 (–CH$_2$–); $^{29}$Si NMR $\delta$ (CDCl$_3$) 33.1. Anal. Calc. for C$_{12}$H$_{27}$ClSi: C, 61.36; H, 11.59. Found: C, 61.33; H, 11.60.

### 3.2.6. cyclo-Hex$_3$SiOMe (run 6)

A mixture of 15.4 g (50 mmol) of $cyclo$-Hex$_3$SiOMe, 37.5 g (360 mmol) of 35% aqueous HCl, and 85 ml of THF was stirred at room temperature for 4 h. The organic layer was separated and analyzed by GLC technique using octadecane as an internal standard as being $cyclo$-Hex$_3$SiCl (99% yield). The organic layer was recrystallized from hexane to give 14.1 g (90% yield) of $cyclo$-Hex$_3$SiCl: m.p. 101–102 °C. All spectral data obtained for $cyclo$-Hex$_3$SiCl are identical with those of the authentic sample reported previously [15].

### 3.2.7. cyclo-Hex$_3$SiOBu-n (run 7)

A mixture of 1.75 g (5.0 mmol) of $cyclo$-Hex$_3$SiOBu-$n$, 3.75 g (36 mmol) of 35% aqueous HCl, and 8.6 ml of

THF was stirred at room temperature for 4 h. The organic layer was separated and analyzed by GLC technique using octadecane as an internal standard as being $cyclo$-Hex$_3$SiCl (98% yield).

### 3.2.8. i-Pr$_2$MeSiOMe (run 8)

To 50.0 g (0.48 mol) of 35% aqueous HCl was added 16.0 g (0.10 mol) of $i$-Pr$_2$MeSiOMe at 0 °C. After the mixture was stirred at 0 °C for 2 h, the organic layer was separated, and analyzed by GLC technique using dodecane as an internal standard as being $i$-Pr$_2$MeSiCl (99% yield). The organic layer was distilled under reduced pressure to give 14.6 g (89% yield) of $i$-Pr$_2$MeSiCl (b.p. 82–83 °C/35 Torr). All spectral data obtained for $i$-Pr$_2$MeSiCl are identical with those of the authentic sample reported previously [16].

### 3.2.9. sec-Bu$_2$MeSiOMe (run 9)

To 50.0 g (0.48 mol) of 35% aqueous HCl was added 18.8 g (0.10 mol) of $sec$-Bu$_2$MeSiOMe at 0 °C. After the mixture was stirred at 0 °C for 2 h, the organic layer was separated, and analyzed by GLC technique using dodecane as an internal standard as being $sec$-Bu$_2$MeSiCl (99% yield). The organic layer was distilled under reduced pressure to give 16.3 g (85% yield) of $sec$-Bu$_2$MeSiCl: b.p. 81–82 °C/15 Torr; MS $m/z$ 192 (M)$^+$; $^1$H NMR $\delta$ (CDCl$_3$) 0.30 (s, 3 H, Me–Si), 0.84–0.93 (m, 2H, HC–Si), 0.95–1.06 (m, 12H, H$_3$C–C–C–CH$_3$), 1.16–1.31, (m, 2H, –CH$_2$–), 1.56–1.76, (m, 2H, –CH$_2$–); $^{13}$C NMR $\delta$ (CDCl$_3$) −3.74, −3.65, −3.6 (Me–Si), 12.8, 12.88, 12.90 (CH$_3$), 13.1, 13.15, 13.17 (CH$_3$), 21.8, 21.87, 21.91 (CH–Si), 23.8, 23.86, 23.88 (–CH$_2$–); $^{29}$Si NMR $\delta$ (CDCl$_3$) 35.0. Anal. Calc. for C$_9$H$_{21}$ClSi: C, 56.07; H, 10.98. Found: C, 56.10; H, 10.99.

### 3.2.10. cyclo-Hex$_2$MeSiOMe (run 10)

To 50.0 g (240 mol) of 35% aqueous HCl was added 12.0 g (50 mmol) of $cyclo$-Hex$_2$MeSiOMe at 0 °C. After the mixture was stirred at 0 °C for 2 h, the organic layer was separated, and analyzed by GLC technique using tetradecane as an internal standard as being $cyclo$-Hex$_2$MeSiCl (99% yield). The organic layer was distilled under reduced pressure to give 10.2 g (83% yield) of $cyclo$-Hex$_2$MeSiCl: b.p. 138 °C/6 Torr; MS $m/z$ 244 (M)$^+$; $^1$H NMR $\delta$ (CDCl$_3$) 0.27 (s, 3H, Me–Si), 0.87–0.96 (m, 2H, HC–Si), 1.22–1.25 (m, 10H, –CH$_2$–), 1.72–1.79, (m, 10H, –CH$_2$–); $^{13}$C NMR $\delta$ (CDCl$_3$) −4.2 (Me–Si), 25.9 (CH–Si), 26.6, 26.66, 26.72, 27.65, 27.69 (–CH$_2$–); $^{29}$Si NMR $\delta$ (CDCl$_3$) 34.0. Anal. Calc. for C$_{11}$H$_{25}$ClSi: C, 63.76; H, 10.29. Found: C, 63.80; H, 10.32.

### 3.2.11. i-PrMe$_2$SiOMe (run 11)

To 25.0 g (240 mmol) of 35% aqueous HCl was added a solution of 1.32 g (10 mmol) of $i$-PrMe$_2$SiOMe in 5.8 ml of xylene at 0 °C over a period of 1 h. After the mixture was stirred for 1 h, the organic layer was separated and

analyzed by GLC using decane as an internal standard, as being *i*-PrMe₂SiCl (97% yield).

### 3.2.12. sec-BuMe₂SiOMe (run 12)

To 25.0 g (240 mmol) of 35% aqueous HCl was added a solution of 1.46 g (10 mmol) of *sec*-BuMe₂SiOMe in 5.8 ml of toluene at 0 °C over a period of 1 h. After the mixture was stirred for 1 h, the organic layer was separated and analyzed by GLC using decane as an internal standard as being *sec*-BuMe₂SiCl (99% yield).

### 3.2.13. cyclo-HexMe₂SiOMe (run 13)

To 25.0 g (240 mmol) of 35% aqueous HCl was added a solution of 1.72 g (10 mmol) of *cyclo*-HexMe₂SiOMe in 5.8 ml of toluene at 0 °C over a period of 1 h. After the mixture was stirred for 1 h, the organic layer was separated and analyzed by GLC using dodecane as an internal standard, as being *cyclo*-HexMe₂SiCl (97% yield).

### 3.2.14. tert-BuMe₂SiOMe (run 14)

To 46.9 g (450 mmol) of 35% aqueous hydrochloric acid was added a solution of 7.3 g (50 mmol) of *tert*-BuMe₂SiOMe in 10 ml of hexane at 0 °C over a period of 1 h. After the mixture was stirred for 2 h, the organic layer was separated and analyzed by GLC using decane as an internal standard, as being *tert*-BuMe₂SiCl (99% yield). The organic layer was distilled to give 5.3 g (71% yield) of *tert*-BuMe₂SiCl (b.p. 124–125 °C). All spectral data obtained for *tert*-BuMe₂SiCl are identical with those of the authentic sample reported previously [17].

### 3.2.15. Et₃SiOMe (run 15)

To 46.9 g (450 mmol) of 35% aqueous hydrochloric acid was added a solution of 7.3 g (50 mmol) of Et₃SiOMe in 10 ml of hexane at 0 °C over a period of 1 h. After the mixture was stirred for 2 h, the organic layer was separated and analyzed by GLC using decane as an internal standard, as being Et₃SiCl (98% yield). The organic layer was distilled to give 5.4 g (72% yield) of Et₃SiCl (b.p. 144–145 °C). All spectral data obtained for Et₃SiCl are identical with those of the authentic sample reported previously [18].

## 3.3. Chlorination of alkoxytrialkylsilanes by hydrogen chloride gas

### 3.3.1. i-PrMe₂SiOMe (run 16)

To a 50-ml four-necked flask fitted with a mechanical stirrer, condenser, inlet tube, and thermometer was placed 6.6 g (50 mmol) of *i*-PrMe₂SiOMe in 29 ml of xylene. hydrogen chloride gas was introduced into the xylene solution at 6–27 °C for 15 min, and the reaction mixture was analyzed by GLC using decane as an internal standard, as being *i*-PrMe₂SiCl (99% yield). The upper layer was distilled to give 3.8 g (55% yield) of *i*-PrMe₂SiCl (b.p. 111 °C). All spectral data obtained for *i*-PrMe₂SiCl

are identical with those of the authentic sample reported previously [19].

### 3.3.2. Chlorination of sec-BuMe₂SiOMe by hydrogen chloride gas (run 17)

To a solution of 7.3 g (50 mmol) of *sec*-BuMe₂SiOMe in 29 ml of toluene was introduced hydrogen chloride gas at 5–18 °C for 25 min. GLC analysis of the reaction mixture using decane as an internal standard showed the presence of *sec*-BuMe₂SiCl in 99% yield. The mixture was distilled to give 4.3 g (57% yield) of *sec*-BuMe₂SiCl (b.p. 134 °C). All spectral data obtained for *sec*-BuMe₂SiCl are identical with those of the authentic sample reported previously [20].

### 3.3.3. Chlorination of cyclo-HexMe₂SiOMe by hydrogen chloride gas (run 18)

To a solution of 8.6 g (50 mmol) of *cyclo*-HexMe₂SiOMe in 29 ml of toluene was introduced hydrogen chloride gas at 5–11 °C for 50 min. The GLC analysis of the reaction mixture using dodecane as an internal standard showed the presence of *cyclo*-HexMe₂SiCl in 99% yield. The mixture was distilled to give 5.2 g (59% yield) of *cyclo*-HexMe₂SiCl (b.p. 98 °C/41 Torr). All spectral data obtained for *cyclo*-HexMe₂SiCl are identical with those of the authentic sample reported previously [21].

## 3.4. Grignard coupling, followed by treatment with 35% aqueous HCl

### 3.4.1. Reaction of MeSiCl₃ with i-PrMgCl, followed by treatment with 35% aqueous HCl (run 19)

In a 300-ml four-necked flask fitted with a mechanical stirrer, condenser, dropping funnel, and thermometer was placed 200 ml (2.4 M, 0.48 mol) of an *i*-PrMgCl–THF–toluene solution (THF/toluene = 1/1). To this was added 17.9 g (0.12 mol) of MeSiCl₃ over a period of 15 min at 80–90 °C. The mixture was heated at 90 °C for 9 h, and then hydrolyzed with 60.0 g (0.58 mol) of 35% HCl aqueous solution. The organic layer was separated, and to this was added 60.0 g (0.58 mol) of 35% aqueous HCl. The mixture was stirred for 1 h with ice-cooling. The organic layer was separated and analyzed by GLC using undecane as an internal standard, as being *i*-Pr₂MeSiCl (73% yield). The organic layer was fractionally distilled to give 11.5 g (59% yield) of *i*-Pr₂MeSiCl (b.p. 82–83 °C/35 Torr).

### 3.4.2. Reaction of Me₂SiCl₂ with i-PrMgCl, followed by treatment with 35% aqueous HCl (run 20)

To 30 ml (2.4 M, 71 mmol) of an *i*-PrMgCl–THF solution was added 6.2 g (48 mmol) of Me₂SiCl₂ over a period of 5 min at 8–13 °C. The mixture was heated at 69 °C for 4 h. To this was added 30 ml of xylene, and then 30 ml of solvents was distilled off from the reaction mixture, and then hydrolyzed with 120.0 g (1.15 mol) of 35% aqueous HCl. The organic layer was separated, and once again 120.0 g (1.15 mol) of 35% aqueous HCl was added to this

layer. The mixture was stirred for 1 h with ice-cooling. The organic layer was separated and analyzed by GLC using decane as an internal standard, as being $i$-PrMe$_2$SiCl (80% yield). The organic layer was fractionally distilled to give 4.2 g (64% yield) of $i$-PrMe$_2$SiCl (b.p. 111 °C).

### 3.4.3. Reaction of Me$_2$SiCl$_2$ with sec-BuMgCl, followed by treatment with 35% aqueous HCl (run 21)

To 50 ml (2.5 M, 127 mmol) of a *sec*-BuMgCl–THF solution was added 5.6 g (43 mmol) of Me$_2$SiCl$_2$ over a period of 1 min. at 11 °C. The mixture was heated at 73 °C for 6 h. After addition of 50 ml of toluene, 50 ml of the solvents was distilled off from the reaction mixture, and then hydrolyzed with 107.5 g (1.03 mol) of 35% aqueous HCl. The organic layer was separated, and 107.5 g (1.03 mol) of 35% aqueous HCl was added to this layer. The mixture was stirred for 1 h with ice-cooling. The organic layer was separated and analyzed by GLC using decane as an internal standard, as being *sec*-BuMe$_2$SiCl (79% yield). The organic layer was fractionally distilled to give 4.1 g (63% yield) of *sec*-BuMe$_2$SiCl (b.p. 134 °C).

### 3.4.4. Reaction of Me$_2$SiCl$_2$ with cyclo-HexMgCl, followed by treatment with 35% aqueous HCl (run 22)

To 50 ml (2.4 M, 119 mmol) of a *cyclo*-HexMgCl–THF solution was added 5.2 g (41 mmol) of Me$_2$SiCl$_2$ over a period of 1 min. at 11 °C. The mixture was heated at 79 °C for 5 h. After addition of 50 ml of toluene, 50 ml of the solvents was distilled off from the reaction mixture, and then hydrolyzed with 106.8 g (0.98 mol) of 35% aqueous HCl. The organic layer was separated, and once again 106.8 g (0.98 mol) of 35% aqueous HCl was added to this layer. The mixture was stirred for 1 h with ice-cooling. The organic layer was separated and analyzed by GLC using dodecane as an internal standard, as being *cyclo*-HexMe$_2$-SiCl (74% yield). The organic layer was fractionally distilled to give 4.3 g (60% yield) of *cyclo*-HexMe$_2$SiCl (b.p. 98 °C/40 Torr).

### 3.5. Chlorination of trialkylsilanols by 35% aqueous hydrochloric acid

### 3.5.1. Et$_3$SiOH (run 23)

To 9.4 g (90 mmol) of 35% aqueous HCl was added 1.32 g (10 mmol) of Et$_3$SiOH in 2 ml of hexane at 0 °C over a period of 1 h. After the mixture was stirred at 0 °C for 2 h, the organic layer was separated and analyzed by GLC using decane as an internal standard, as being Et$_3$SiCl (96% yield).

### 3.5.2. i-Pr$_3$SiOH (run 24)

In a 50-ml four-necked flask fitted with a mechanical stirrer, condenser, and thermometer were placed 8.7 g (50 mmol) of $i$-Pr$_3$SiOH and 15.6 g (150 mmol) of 35% aqueous HCl. After the mixture was stirred at room temperature for 2 h, the organic layer was separated and analyzed by GLC using tridecane as an internal standard, as

being $i$-Pr$_3$SiCl (99% yield). The organic layer was distilled under reduced pressure to give 9.2 g (95% yield) of $i$-Pr$_3$SiCl (b.p. 78–80 °C/10 Torr).

### 3.5.3. tert-BuMe$_2$SiOH (run 25)

To 9.4 g (90 mmol) of 35% aqueous HCl was added 1.32 g (10 mmol) of *tert*-BuMe$_2$SiOH in 2 ml of hexane at 0 °C over a period of 1 h. After the mixture was stirred at 0 °C for 2 h, the organic layer was separated and analyzed by GLC using decane as an internal standard, as being *tert*-BuMe$_2$SiCl (98% yield).

### 3.5.4. tert-BuPh$_2$SiOH (run 26)

A mixture of 2.56 g (10 mmol) of *tert*-BuPh$_2$SiOH, 3.1 g (30 mmol) of 35% aqueous HCl, and 12.8 ml of THF was stirred at 40 °C for 4 h, the organic layer was separated and analyzed by GLC using pentadecane as an internal standard, as being *tert*-BuPh$_2$SiOH (98% yield).

### 3.6. Chlorination of trialkylsilanes with 35% aqueous HCl in the presence of a Pd catalyst

### 3.6.1. Chlorination of i-Pr$_3$SiH in the presence of a PdCl$_2$ catalyst (run 27)

In a 50-ml four-necked flask fitted with a mechanical stirrer, condenser, and thermometer were placed 7.9 g (50 mmol) of $i$-Pr$_3$SiH, 15.6 g (150 mmol) of 35% aqueous HCl, and 0.088 g (1.0 mol%) of PdCl$_2$. The mixture was stirred at room temperature for 3 h. The organic layer was separated and distilled under reduced pressure to give 9.1 g (95% yield) of $i$-Pr$_3$SiCl (b.p. 78–80 °C/10 Torr).

### 3.6.2. Chlorination of i-Pr$_3$SiH in the presence of a Pd/C catalyst (run 28)

To a mixture of 15.6 g (150 mmol) of 35% aqueous HCl, and 2.29 g (1.0 mol%) of 2.3% Pd/C was added 7.9 g (50 mmol) of $i$-Pr$_3$SiH. The mixture was stirred at room temperature for 3 h, and then the palladium catalyst was filtered off. The organic layer was separated and distilled under reduced pressure to give 5.5 g (57% yield) of $i$-Pr$_3$SiCl (b.p. 78–80 °C/10 Torr).

To a mixture of 15.6 g (150 mmol) of 35% aqueous HCl and the recovered Pd catalyst was added 7.9 g (50 mmol) of $i$-Pr$_3$SiH. The mixture was stirred at room temperature for 3 h, and then the palladium catalyst was filtered off. The organic layer was separated and distilled under reduced pressure to give 9.5 g (99% yield) of $i$-Pr$_3$SiCl (b.p. 78–80 °C/10 Torr).

### 3.6.3. Chlorination of Et$_3$SiH in the presence of a PdCl$_2$ catalyst (run 29)

To a mixture of 125.0 g (1.2 mol) of 35% aqueous HCl and 0.088 g (1.0 mol%) of PdCl$_2$ was added 5.8 g (50 mmol) of Et$_3$SiH in 8 ml of hexane at 0 °C for 25 min. The mixture was stirred at 0 °C for 2 h. The organic layer was separated and analyzed by GLC using decane as an internal standard, as being Et$_3$SiCl (97% yield). The

organic layer was distilled to give 6.6 g (87% yield) of Et$_3$SiCl (b.p. 144–145 °C).

### 3.6.4. Chlorination of tert-BuMe$_2$SiH in the presence of a PdCl$_2$ catalyst (run 30)

To a mixture of 15.6 g (150 mmol) of 35% aqueous HCl and 0.044 g (0.5 mol%) of PdCl$_2$ was added 5.8 g (50 mmol) of *tert*-BuMe$_2$SiH in 8 ml of hexane at room temperature over a period of 5 min. The mixture was stirred at room temperature for 2 h. The organic layer was separated and analyzed by GLC analysis using decane as an internal standard, as being *tert*-BuMe$_2$SiCl (93% yield). The organic layer was distilled to give 6.3 g (84% yield) of *tert*-BuMe$_2$SiCl (b.p. 124–125 °C).

### 3.6.5. Chlorination of tert-BuMe$_2$SiH in the presence of a Pd/C catalyst (run 31)

To a mixture of 15.6 g (150 mmol) of 35% aqueous HCl and 1.14 g (0.5 mol%) of 2.3% Pd/C was added 5.8 g (50 mmol) of *tert*-BuMe$_2$SiH in 8 ml of hexane at room temperature for 5 min. The mixture was stirred at room temperature for 2 h, and then the palladium catalyst was filtered off. The organic layer was separated and analyzed by GLC using decane as an internal standard, as being *tert*-BuMe$_2$SiCl (79% yield).

To a mixture of 15.6 g (150 mmol) of 35% aqueous HCl and the recovered Pd catalyst was added 5.8 g (50 mmol) of *tert*-BuMe$_2$SiH in 8 ml of hexane at room temperature. After stirring at room temperature for 2 h, the palladium catalyst was filtered off. The organic layer was separated and analyzed by GLC using decane as an internal standard, as being *tert*-BuMe$_2$SiCl (97% yield). The organic layer was distilled to give 6.6 g (87% yield) of *tert*-BuMe$_2$-SiCl (b.p. 124–125 °C).

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