Direct Synthesis of Trisilaalkanes

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A series of trisilaalkanes has been prepared in high yields by the direct reaction of α-chloromethylsilanes with metallic silicon in the presence of copper catalyst using the stirred reactor equipped with a spiral band agitator at the carefully controlled temperature between 280°C and 340°C. Disilaalkane compounds were obtained as the minor products. Cadmium was found to be a good promotor for the reactions, while zinc was an inhibitor.

Introduction

Although the direct synthesis of alkylchlorosilanes from metallic silicon and alkyl chlorides has been extensively studied and a vast number of reports are available in the literature,[1] the reports on the direct reactions of metallic silicon with α-chloromethylsilanes are scarce. In 1956 Petrov et al. reported first the direct reactions of α-chloromethyltrichlorosilane and α-chloromethylmethyldichlorosilane with silicon in the presence of copper catalyst at the temperature 370-390°C using a fixed bed reactor.[2] The yields of the expected trisilaalkane products were very poor, thus giving 8.5% of 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane from α-chloromethyltrichlorosilane and 16.7% of 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane from α-chloromethylmethyldichlorosilane. Mironov et al. reported later the direct synthesis of 2,4,4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane from α-chloromethyldimethylchlorosilane, without mentioning the yield probably due to complex side reactions.[3] The direct reaction of α-chloromethyltrimethylsilane with silicon has never been reported before.

We wish to report the preparation of trisilaalkanes in high yields by reactions of a series of α-chloromethylsilanes with metallic silicon in the presence of copper catalyst at the carefully controlld temperature between 280°C and 340°C using a stirred bed reactor.

Experimental

Reagents and Solvents. α-Chloromethylsilane compounds were either prepared by the photochlorination reaction of the corresponding methylsilane or purchased from Petrarch Chemical Co. α-Chloromethylsilane compounds were purified through distillation under dry nitrogen atmosphere. Cuprous chloride was from Kanto Chemical Co., metallic copper catalysts from American Chemet Co. (Deerfield, IL, U.S.A.) and Alcan Metal Powders (Union, NJ, U.S.A.), zinc powder from Junsei Chemical Co., cadmium power from Aldrich Chemical Co., and lithium aluminum hydride from Janssen Chemical Co. Diethylether and tetrahydrofuran were dried over sodium/benzophenone and distilled before use. Silicon metal was purchased from Samchuck Mining Co. (Kangwon-do, Korea) as a lump and pulverized using the jaw-crusher and the pulverizer. Silicon metal powder between 100-325 mesh size was collected by sieving.

Physical Measurements. The products were analyzed for the composition with gas chromatographic method (Varian 3300, glass capillary column, SE-54, 12 m, equipped with Flame Ionization Detector; or Varian 3300, packed column OV-101, 0.5 m, 1.8″ OD., S.S., equipped with Thermal Conductivity Detector). Structural characterizations were performed by typical spectroscopic techniques such as NMR(Jeol JNM-PMX 60, 60 MHz; Varian Gemini 300, 300 MHz), FT-IR(Analect FX-6160) and GC-MS(Hewlett-Packard GC 5890 and MSD 5970). Elemental analysis was carried out by the Analytical Chemistry Laboratory in Korea Institute of Science and Technology, Seoul, Korea.

Synthesis. The reactor which was used in this experiment was made of Pyrex glass tube, 25 mm inner-diameter and 400 mm length, with the electrical heating wire coiled outside the glass tube. The reactor was set vertically and the bottom was loosely closed with glass beads and glass wool and the stirrer motor was set at the top. The stirrer rod inside the reactor was made of 1/4″ stainless steel tube, 520 mm in length with closed end, with stirrer blade about 20 mm diameter and 300 mm length, coiled with 4 mm stainless steel tube, attached. The thermocouple wire (type K) was placed inside stirrer rod through the hole in the stirrer motor to read the temperature at the middle of the reaction bed (metallic silicon and catalysts) and connected to the automatic temperature controller. Syringe pump (KASP-005/150 MT, Keun-a Mechatronics Co.; with Hamilton gas tight syringe, 50 m*l* size) to add liquid chloromethylsilane reactant was connected to the top of the reactor through Teflon needle. Top of the reactor was also connected to nitrogen gas to push α-chloromethylsilane reactant vapor to the reactor after it was vaporized at the preheater. A 250 m*l* round bottom flask equipped with a condenser and a stopcock at the bottom was attached to the bottom of the reactor as a receiver. Liquid products and unreacted reactant were collected at the receiver and drained into the outside collector.

A mixture of metallic silicon 100g (100-325 mesh) and the copper catalyst (10 wt.% of Cu in Cu and Si mixture) was placed in the reactor and dried at the 180-200°C for 2 hours with stirring with dry nitrogen flush. Then the temperature was raised to 370°C for sintering between metallic silicon and catalyst to give Si-Cu η-phase contact mixture. For catalyst cuprous chloride, sintering process was done under dry nitrogen atmosphere and for some other cases it was done under methyl chloride gas atmosphere. After removing compounds formed during sintering process, the temperature was lowered to 320°C, α-chloromethylsilane reactant was introduced into the reactor at the rate of 10 m*l*/hr with nitrogen flowing at the rate of 60 m*l*/min. About 5 minutes after

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introduction, it was observed that the reaction temperature was raised slightly dut to the exothermic nature of the reaction and then viscous liquid was collected on the receiver. Product was drained at 1 or 2 hour period and analyzed for the compositions by gas chromatographic method. After the reaction all the collected product was fractionally distilled into the individual components and they were analyzed for the structures. Some components were hydrogenated with lithium aluminum hydride in dried diethylether before their structure analysis.

Using the experimental procedure above, α-chloromethyltrimethylsilane, **7** (65.6 g) was allowed to react with silicon in the presence of copper catalyst and cadmium co-catalyst for 8 hours. After the reaction, product mixture (66.8 g) was collected and the composition was analyzed as; 4,4-dichloro-2,2,6,6-tetramethyl-2,4,6-trisilaheptane, **8** (87.5%; bp. 112-115 ℃/9 torr; ¹H-NMR (CCl₄) δ 0.20(s, 18H, CH₃), 0.55(s, 4H, CH₂); ¹³C-NMR(CDCl₃) δ 12.55(-CH₂-), 1.04(-CH₃)), 1,1,1-trichloro-3,3-dimethyl-1,3-disilabutane, **9**, (6.5%; bp. 173-174℃; ¹H-NMR(CCl₄) δ 0.25(s, 9H, CH₃), 0.85(s, 2H, CH₂); ¹³C-NMR (CDCl₃) δ 14.40(-CH₂-), 0.52(-CH₃)), trimethylchlorosilane (0.8 % ; bp. 56℃), tetramethylsilane (3.6%; bp. 28℃).

α-Chloromethyldimethylchlorosilane, **1** (108.5 g) was employed in a same reaction condition for 10.5 hours to give 113.8 g of product mixture and the composition was; 2,4,-4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane³, **2**, (82.2%; bp. 94-95℃/1.5 torr), 1,1,1,3-tetrachloro-3-methyl-1,3-disilabutane³, **3**, (2.3%; bp. 169.5-170℃), 2,4,4,5,5,7-hexachloro-2,7-dimethyl-2,4,5,7-tetrasilaoctane, **4** (trace; ¹H-NMR (CCl₄) δ 0.63(s, 12H, -CH₃), 1.12(s, 4H, -CH₂-); ¹³C-NMR(CDCl₃) δ 4.51 (-CH₃), 12.02(-CH₂-). Compound such as **4** contained many chlorine atoms and was quite unstable due to the high sensitivity of silicon-chlorine bonds toward the moisture. Therefore the elemental analysis could not be made within the reasonable error range. Instead, **4** was reduced with lithium aluminum hydride to 2,7-dimethyl-2,4,5,7-tetrasilaoctane, **5**, for further structure identification. **5**, ¹H-NMR(CDCl₃) δ 4.2-3.8(m, 2H, Si-H), 3.8-3.5(m, 4H, Si-H), 0.15-0.1(d, 12H, -CH₃), 0-−0.3(m, 4H, -CH₂-); ¹³C-NMR(CDCl₃) δ −2.62(-CH₃), −10.61 (-CH₂-); Anal. found (calcd. for C₆H₂₂Si₄): C 32.04(34.88); H 10.41(10.73)), 2,4-dichloro-2,4-dimethyl-2,4-disilapentane³, **6** (trace), trimethylchlorosilane (9.1%), dimethyldichlorosilane (1.5%; bp. 70℃).

α-Chloromethylmethyldichlorosilane, **10** (139.4 g) was employed in a same reaction condition for 13 hours to give 144.7 g of product mixture and the composition was; 2,2,4,-4,6,6-hexachloro-2,4,6-trisilaheptane², **11**, (60.6%; bp. 97-97.5 ℃/1.5 torr; 123-124℃/3 torr²), 1,1,1,3,3,-pentachloro-1,3-disilabutane², **12** (19.1%; bp. 181.5-182℃; 183.5-184.5℃²), 2,2,4,-4,5,5,7,7-octachloro-2,4,5,7-tetrasilaoctane, **13**, (4.3%; ¹H-NMR (CDCl₃) δ 1.47(s, 4H, -CH₂-), 0.99(s, 6H, -CH₃); ¹³C-NMR (CDCl₃) δ 15.18(-CH₂-), 7.96(-CH₃); after reduction to 2,4,5,7-tetrasilaoctane, **14**, ¹H-NMR(CDCl₃) δ 3.89-3.82(h, 4H, Si-H), 3.68-3.63(m, 4H, Si-H), 0.23-0.2(t, 6H, -CH₃), 0.01- −0.04(p, 4H, -CH₂-); ¹³C-NMR(CDCl₃) δ −6.52(-CH₃), −14.67(-CH₂-)), 6-methyl-2,2,4,4,6,8,8-heptachloro-2,4,6,8-tetrasilanonane, **15**, (3.8%; ¹H-NMR(CDCl₃) δ 1.38(s, 2H, -CH₂-), 1.17(s, 2H, -CH₂-), 1.07(s, 2H, -CH₂-), 0.95(s, 3H, -CH₃), 0.9(s, 3H, -CH₃), 0.74(s, 3H, -CH₃); ¹³C-NMR(CDCl₃) δ 18.33(-CH₂-), 15.12 (-CH₂-), 14.86(-CH₂-), 8.02(-CH₃), 7.71(-CH₃), 5.01(-CH₃); after reduction to 6-methyl-2,4,6,8-tetrasilanonane, **16**, ¹H-NMR

(CDCl₃) δ 4.02-4.05(m, 1H, Si-H), 3.9-3.85(m, 2H, Si-H), 3.86-3.8(m, 4H, Si-H), 0.21-0.17(m, 9H, -CH₃), 0- −0.09(m, 6H, -CH₂-); ¹³C-NMR(CDCl₃) δ −2.47(-CH₃), −5.1(-CH₃), −5.5 (-CH₃), −6.1(-CH₂-), −6.5(-CH₂-), −9.48(-CH₂-)), 2,2,4,4-tetrachloro-2,4-disilapentane², **17**, (1.2%), dimethyldichlorosilane (4.9%). Elemental analysis could not be made within reasonable range with **14** and **16** due to the unstability.

α-Chloromethyltrichlorosilane, **18** (38.0 g) was employed in a same reaction condition for 4 hours to give 39.9 g of product mixture and the composition was; 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane², **19**, (50.7%; bp. 83.5-85℃/2 torr; 157-158℃/6 torr²), 1,1,1,3,3,3-hexachloro-1,3-disilapropane², **20**, (13.7%; bp. 173-174℃; 179.9℃²), 1,1,1,3,3,4,4,6,6,6-decachloro-1,3,4,6-tetrasilahexane, **21**, (16.9%; ¹H-NMR(CDCl₃) δ 1.76(s, -CH₂-); ¹³C-NMR(CDCl₃); δ 17.67(-CH₂-); after reduction to 1,3,4,6-tetrasilahexane, **22**, ¹H-NMR(CDCl₃) δ 3.72-3.66 (m, 10H, Si-H), 0.05- −0.02(m, 4H, -CH₂-); ¹³C-NMR(CDCl₃) δ −19.93(-CH₂-), Anal. found(calcd. for C₂H₁₄Si₄): C 15.33 (15.96), H 9.26(9.37), 1,1,1,3,3,5,5,7,7,7-decachloro-1,3,5,7-tetrasilaheptane, **23**, (5.9%; ¹H-NMR(CDCl₃) δ 1.71(s, 4H, -CH₂-), 1.54(s, 2H, -CH₂-); ¹³C-NMR(CDCl₃) δ 20.47(-CH₂-). 17.56 (-CH₂-); after reduction to 1,3,5,7-tetrasilaheptane, **24**, ¹H-NMR(CDCl₃) δ 3.95-3.86(p, 4H, Si-H), 3.65-3.62(t, 6H, Si-H), 0.08-0.02(n, 2H, -CH₂-), 0.03- −0.03(h, 4H, -CH₂-); ¹³C-NMR (CDCl₃) δ −9.8(-CH₂-), −15.25(-CH₂-, terminal)), methyltrichlorosilane (2.6%; bp. 66℃). Elemental analysis could not be made within reasonable range with **24** due to the unstability.

Results and Discussion

Reactor. The direct synthesis is the most widely used industrial method for the preparations for methylchlorosilanes.[4] The direct process can be carried out either in fixed bed[5], in stirred bed[6], or in fluidized bed[7] reactors. The process with the stirred bed reactors has the advantages over the fixed bed operation in that the heat of reaction can be removed more easily and the movement of the powders causes fresh surface to be continuously exposed.[8] The metal powder was agitated in an up and down motion in a vertical reactor by means of spiral band rotated by a central shaft while a stream of methyl chloride was upward through it.[9]

As the reaction rate and the composition of the products in the direct process are known to be highly temperature-dependent,[10] it is much important to maintain the reaction temperature at an accurately specified temperature and to prevent any hot spot developing in the agglomerates of the solid phase. It is reported that at higher temperatures, the deposition of carbon on the surface of the metal mixture occurs, which decreases the reactivity and the selectivity as well.[11] This is why the reactor for the direct synthesis of methylchlorosilane must have a high thermal stability and an efficient heat transfer.

The diagram of the stirred reactor, equipped with a spiral band agitator used for the direct synthesis of trisilaalkanes is shown in Figure 1. 100g of silicon powder between 100 mesh and 325 mesh was used. The α-chloromethylsilanes were added dropwise from the top of the reactor using a syringe pump to the preheater kept at 250℃. The high boiling products of trisilaalkanes were withdrawn from the bottom of the reactor. Some addition of inert gases such as
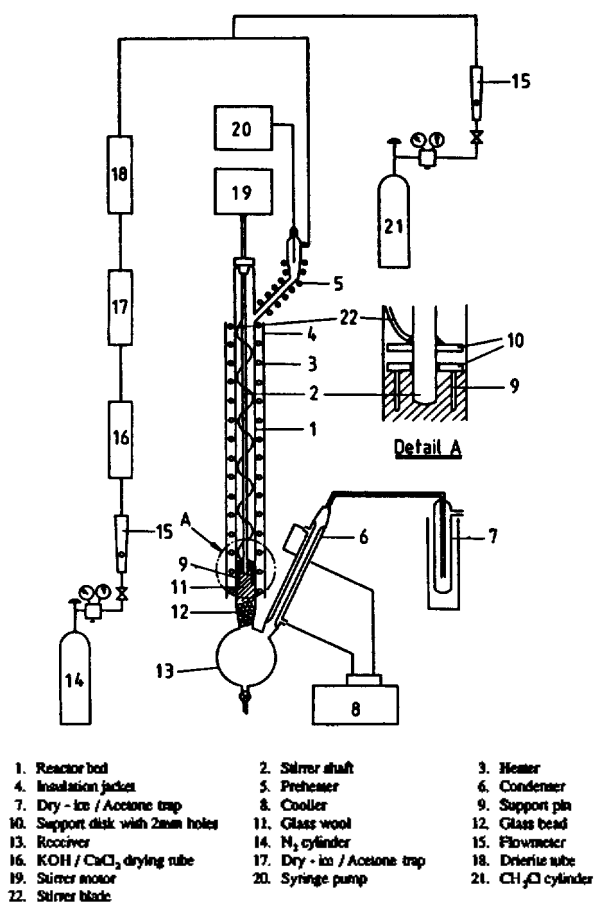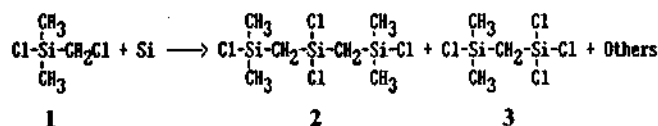
Figure 1. Stirred reactor for direct synthesis of trisilaalkanes.

1. Reactor bed	2. Stirrer shaft	3. Heater
4. Insulation jacket	5. Preheater	6. Condenser
7. Dry-ice / Acetone trap	8. Cooler	9. Support pin
10. Support disk with 2mm holes	11. Glass wool	12. Glass bead
13. Receiver	14. N₂ cylinder	15. Flowmeter
16. KOH / CaCl₂ drying tube	17. Dry-ice / Acetone trap	18. Drierite tube
19. Stirrer motor	20. Syringe pump	21. CH₂Cl cylinder
22. Stirrer blade		

nitrogen or argon to the starting material was helpful to blow the starting silane into the reactor and then the products out of the reactor to the condenser at the bottom.

Reaction Temperature. α-Chloromethyldimethylchlorosilane, 1 was reacted with silicon in the presence of CuCl as the catalyst at the temperature between 280°C and 340°C.

CuCl is the most commonly used catalyst in laboratory experiments because of the easiness to prepare the contact mixture.[12] The product distributions from the direct reaction of 1 with metallic silicon in the presence of CuCl as the catalyst at various reaction temperatures are shown in the Table 1.

$$\underset{\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Cl-Si-CH_2Cl}}}{} + Si \longrightarrow \underset{\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Cl-Si-CH_2}}}{} \underset{\underset{\overset{|}{Cl}}{\overset{\overset{Cl}{|}}{Si-CH_2}}}{} \underset{\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Si-Cl}}}{} + \underset{\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Cl-Si-CH_2}}}{} \underset{\underset{\overset{|}{Cl}}{\overset{\overset{Cl}{|}}{Si-Cl}}}{} + Others$$

$$\quad\quad 1 \quad\quad\quad\quad\quad\quad 2 \quad\quad\quad\quad\quad 3$$

As shown in the Table 1, the significant amount of the starting compound 1 was recovered when the reaction temperature was below 300°C, while the reaction went to completion above 320°C. The yield of 2,4,4,6-tetrachloro-2,4,6-trisilaheptane, 2, was generally higher than that of 3-methyl-1,1,1,3-tetrachloro-1,3-disilabutane, 3, except for the reaction at 340°C. The highest selectivity of 54.2% for 2 was obtained at the reaction temperature of 320°C. However, the selectivity was still much lower compared with that over 90% for dimethyldichlorosilane in the direct reaction of methylchloride with silicon in the presence of copper catalyst.[13] Besides the products 2 and 3 several other minor by-products were also obtained. The total amount of the minor products increased as the reaction temperature increased suggesting that the decomposition of 1 occurred more at higher reaction temperatures.

Catalyst and Co-catalyst. Useful copper catalysts for the reaction between alkylchloride and silicon include copper metal, copper salts and partially oxidized copper.[1] A copper content of 5-10%, normally used in the direct synthesis of methylchlorosilanes, leads to the highest conversion of methylchloride to dimethyldichlorosilane. In addition to copper catalyst, a number of metals such as zinc, aluminum, magnesium, etc. were used as promoters. The promoters were normally incorporated in smaller quantity than 1%. The product distributions from the reaction of 1 with silicon in the presence of different catalyst and co-catalysts are shown in Table 2.

Table 1. The Results of the Direct Synthesis at Various Reaction Temperature

Exp. #	Reaction temp. (°C)	Reactant (g)	R_{xn} Time (hrs)	Product (g)	Yields (%) 2	3	Others	React. recovd. (%)
1	340	139.2	13.0	139.6	22.9	33.3	43.0	0.8
2	320	189.6	18.5	198.6	54.2	12.7	33.1	0
3	300	126.7	12.0	129.4	32.7	19.2	25.3	22.8
4	280	145.0	13.0	145.7	32.7	26.6	28.1	12.6

Table 2. The Effect of the Catalysts and Co-catalysts on the Direct Synthesis*

Exp. #	Reactant amount (g)	Catalyst/ Co-catalyst	R_{xn} Time (hrs)	Product (g)	Yields (%) 2	3	Others	React. recovd. (%)
2	189.6	CaCl	18.5	198.6	54.2	12.7	33.1	0
5	366.8	Cu	37.0	387.2	51.2	9.0	8.9	30.9
6	49.4	Cu/Zn	5.0	49.2	trace	7.8	30.1	62.1
7	108.5	Cu/Cd	10.5	113.8	82.2	2.5	15.3	0

*Reaction temperature was 320°C
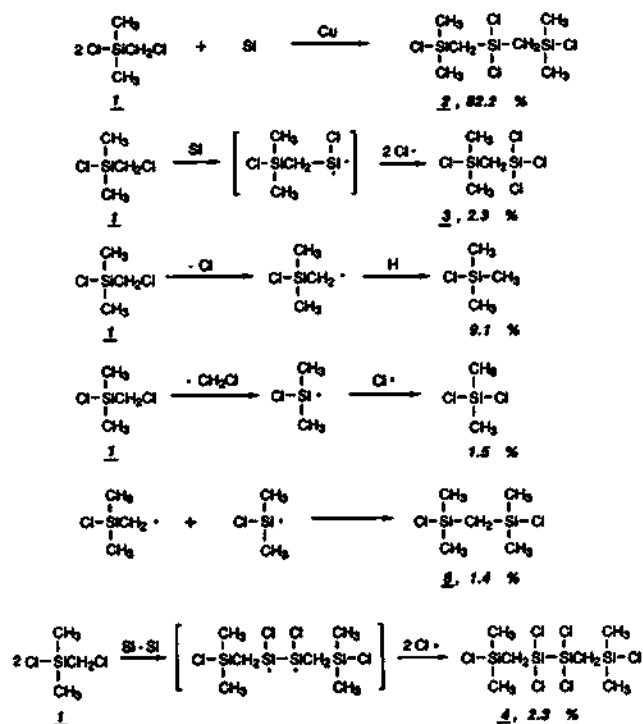
Scheme 1. Possible mechanisms for the direct synthesis

In Exp. #5, the commercially available copper catalysts[14] for the reaction between silicon and methyl chloride was used. It is interesting to note that 30.9% of the starting 1 was recovered in Exp. #5 as compared with no recovery in Exp. #2. This indicates that the catalytic activity of CuCl is higher than the commercial catalyst. The selectivity for 2 was about the same for two cases. However, the amount of the by-products due to the decomposition of 1 is much lower in Exp. #5 than Exp. #2. It is surprizing that the addition of only 0.5% zinc of the total solid mass deactivates the reaction significantly in Exp. #6; 2 is obtained in trace amount, while 62.1% of the starting 1 is recovered. Zinc is known as a good promoter for the direct synthesis of methylchlorosilanes[15] and has been also claimed previously for the reaction between α-chloromethylsilanes and silicon.[16] Zinc is found to be an inhibitor rather than promotor in this work. In contrast to zinc addition, cadmium enhanced the reactivity and the selectivity as well. 82.2% of 2 was obtained and no starting 1 was recovered in Exp. #7.

The Characterization of the Minor Products. In the

reaction of methylchloride with silicon, dimethyldichlorosilane is not the only product, but methyltrichlorosilane, trimethylchlorosilane, tetrachlorosilane, tetramethylsilane, methyldichlorosilane and methylchlorosilanes containing more than one silicon atom are also obtained. In addition, a considerable amount of gaseous decomposition products such as hydrogen, methane, ethane, ethylene, etc. was formed.[4] Several minor products beside 2 and 3 were also obtained from the reaction of 1 with metallic silicon. All the products including minor by-products from Exp. #7 were isolated and characterized. Their structure and the yields are listed in the Scheme 1 along with the possible mechanisms. This indicates that the reaction of 1 with silicon consists of a number of parallel reactions.

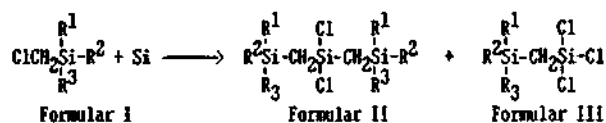The first five compounds from the top in the Scheme 1 are known and have been reported in the literature.[3] 2 is the expected product from the coupling reaction of two moles of 1 with one silicon atom. It appeared from the kinetics[1] of the reaction of methyl chloride with a silicon-copper alloy that the first step is dissociative adsorption of chloromethyl group of 1 on the active center of the solid surface, giving an orientation of Si···CH₂R and Cu···Cl. The next step may be the transfer of a chlorine from the copper to the silicon completing RCH₂−Si−Cl bond, but this may be preceded by adsorption of a second molecule of 1, thereby having two molecules of 1 coupled with one silicon to give 2. The formation of 3 can be explained by the reaction of one mole of 1 with one silicon atom and followed by chlorine abstraction. Trimethylchlorosilane may be explained by chlorine splitting from chloromethyl group of 1 and followed by hydrogen abstraction by the resulted silylmethyl radical. Dimethyldichlorosilane can be explained by chloromethyl group splitting from 1 followed by chlorine abstraction by the resulting silyl radical. 2,4-Dimethyl-2,4-dichloro-2,4-disilapentane, 6, is formed from the coupling reaction of the above metioned silylmethyl and silyl radicals. 2,4,4,5,5,7-Hexachloro-2,7-dimethyl-2,4,5,7-tetrasilaoctane, 4, is an analogy of 2 except the extra dichlorosilylene group in the middle of the molecule. This may be due to that each one of 1 reacted with each of two connected silicon atoms and followed by chlorine abstraction by the resulting intermediate. Trace amounts of other products detected on GC were not collected.

The Reactivity and Selectivity of α-chloromethylsilanes. The reaction was extended to other α-chloromethylsilanes and the results are shown in Table 3 along with the literature data.

Table 3. The Results of the Direct Reactions of α-Chloromethylsilanes*

Exp. #		Reactant			Amt (g)	R_{xn} Time (hrs)	Product (g)	II		III		Others	Remark
		R^1	R^2	R^3									
2	7	Me	Me	Me	65.6	8.0	66.8	8,	87.5	9,	6.5	6.0	This work
7	1	Me	Me	Cl	108.5	10.5	113.8	2,	82.2	3,	2.3	15.5	This work
									some		some		Ref. 3
8	10	Me	Cl	Cl	139.4	13.0	144.7	11,	60.7	12,	19.1	20.4	This work
									16.7		28.7		Ref. 2
9	18	Cl	Cl	Cl	38.0	4.0	39.9	19,	50.7	20,	13.7	35.6	This work
									8.5		30.0		Ref. 2

*Reaction temperature was 320℃.

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Formular I   Formular II   Formular III

wherein R^1, R^2, R^3 may independantly be Cl or methyl.

As shown in Table 3, trisilaalkanes, Formular II, were obtained in much higher yields compared with the literature values. The highest selectivity for trisilaalkanes was obtained from the reaction of α-chloromethyltrimethylsilane, **7**, and the lowest from α-chloromethyltrichlorosilane, **18**. Higher amount of by-products were obtained from the reaction of highly chlorinated silanes, while smaller amount of by-products from highly methyllated silanes.

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Contribution of Electrophilic Interference on Solvolytic Reactions in Fluorinated Alcohol Mixtures

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The degree of electrophilic interference on the solvolytic reactions of model substrates has been studied in fluorinated alcohol solvent mixtures. With variation of solvent composition of 1,1,1,3,3,3-hexafluoro-2-propanol(HFP) and 2-propanol (PrOH) mixtures, the magnitude of electrophilic solvent assistance was changed inversely with the degree of nucleophilic solvent assistance. The contribution of electrophilic interference for 2-adamantyl tosylate showed higher than *tert*-butyl chloride in HFP-PrOH mixtures. Through a correlation of nucleophilic solvent assistance and electrophilic solvent assistance based on the method of double differences, HFP-PrOH mixture showed a big discrepancy from non-fluorinated alcohol systems.

Introduction

Solvent nucleophilicity has been of considerable interest in the study of solvent effect[1]. In particular, weak nucleophilic media such as carboxylic acids or fluorinated alcohols are well recognized to show a very different solvent effect comparing with the hydroxylic solvents such as water and alcohols in various solvent-assisted reactions.[1b] Carboxylic acids and fluorinated alcohols show a weak nucleophilic property in the solvolytic reactions of the model substrate of

tert-butyl chloride[2] and 2-adamantyl tosylate[3]. Fluorinated alcohols which are substituted fluorine instead of hydrogen should exhibit a very weak acidity[4]. Weak acidity of fluorinated alcohols are considerably sensitive to the nucleophilic solvent-assisted reactions.

Solvent properties were investigated widely for trifluoroethanol(TFE)[5] and 1,1,1,3,3,3-hexafluoro-2-propanol(HFP)[6] in order to determine their nucleophilicity(N) and ionizing power(Y) in many fluorinated alcohols. TFE and HFP are shown different solvent effect by nucleophilic solvent assist-