Grignard Coupling Reaction of Bis(chloromethyl)diorganosilanes with Dichloro(diorgano)silanes: Syntheses of 1,3-Disilacyclobutanes

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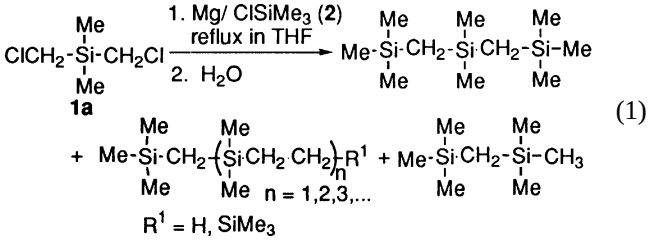
The Grignard coupling reaction of bis(chloromethyl)diorganosilanes [$(ClCH_2)_2SiR^1R^2$: $R^1 = R^2 = Me$, **1a**; $R^1 = Me$, $R^2 = Ph$, **1b**; $R^1 = R^2 = Ph$, **1c**] with diorganodichlorosilanes [$(Cl_2SiR^3R^4$: $R^3 = R^4 = Me$, **2a**; $R^3 = Me$, $R^4 = Ph$, **2b**; $R^3 = R^4 = Ph$, **2c**] at THE reflux temperature gave the intermolecular C-Si coupling product of 1,1,3,3-tetraorgano-1,3-disilacyclobutanes **3a-f** in poor to moderate yields ranging from 7% to 50% along with polydiorganosilapropanes. The cyclization reaction of **1a-c** with methyl-substituted dichlorosilanes **2a, b** gave 1,3-disilacyclobutanes **3a-c**, **e**, **d** in moderate yields (42–50%), while the same reaction with dichlorodiphenylsilane (**2c**) to 1,3-disilacyclobutanes **3d**, **f** resulted in low yield (7–18%) probably due to the steric hindrance of two-phenyl groups on the silicon of **2c**.

Introduction

Polycarbosilanes have been used as important precursors for silicon carbide, a high performance fine ceramic.[1] 1,3-Disilacyclobutanes are potential starting materials for polycarbosilanes, since 1,3-disilacyclobutanes undergo a ring-open polymerizations to give polycarbosilanes in the presence of platinum or other metal catalysts.[2-4] Several synthetic routes for 1,3-disilacyclobutanes such as the bimolecular condensation of (chloromethyl)chlorosilanes,[5] the Grignard coupling of bis(chloromethyl)silanes with dichlorosilanes,[6] and the pyrolysis of bis(trimethylsilylmethyl) alkoxysilanes[7] have been reported, but known to be low efficient processes in the viewpoint of economical production.

Bis(chloromethyl)dichlorosilane have been produced as a byproduct in large quantity by the photochlorination[8] of dichlorodimethylsilane to give (chloromethyl)dichloromethylsilane used as a starting material for flusilazole.[9] The application of byproducts have been relatively unexplored in the field of organosilicon chemistry. The cyclization reaction of bis(chloromethyl)dimethylsilane with dichlorosilanes or dichlorogermanes using magnesium or lithium has been reported by Seyferth to give 1,3-disilacyclobutanes or 1-sila-3-germacyclobutanes, respectively, in low yields ranging from 21% to 24% due to the production of unidentified polymeric materials.[6]

Recently we reported that the reaction of bis(chloromethyl)silanes with Mg at THF reflux temperature gave poly(silapropanes) in 80–90% yields.[10] The formation of poly(silapropanes) was explained by the ring-opening polymerization of the silacyclopropane intermediate generated by intramolecular cyclization of the mono Grignard reagent. We also have studied the Grignard coupling reaction of bis(chloromethyl)silanes with trimethylchlorosilane.[11] In this reaction, both the intramolecular C-C coupling and the intermolecular C-Si coupling reactions were competing. As the mole ratio of trimethylchlorosilane with respect to bis(chloromethyl)dimethylsilane was increased, the yields of the intermolecular C-Si coupling products was increased while the undesired poly(diorganosilapropanes) was decreased.[11] This suggests that the Grignard coupling reaction of bis(chloromethyl)silanes with diorganodichlorosilane might be a good synthetic route for 1,3-disilacyclobutanes



(1)

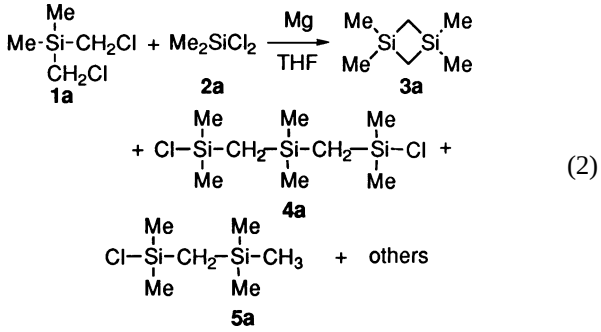
with a various substituents on silicon.

We wish to report the intermolecular C–Si coupling reaction of bis(chloromethyl)diorganosilanes (**1**) with dichlorodiorganosilanes (**2**), leading to 1,3-disilacyclobutanes.

Results and Discussion

Product Distributions and Mole Ratio of 2a respect to 1a. Since both the intramolecular C–C coupling and the intermolecular Si–C coupling are competing in the Grignard reaction of bis(chloromethyl)dimethylsilane (**1a**) with chlorosilanes, we have focused to optimize the intermolecular cyclization reaction of **1a** with dimethyldichlorosilane (**2a**) to afford 1,3-disilacyclobutane. At first, the Grignard coupling reaction of simple **1a** with **2a** as representative starting materials at the reflux temperature of THF was carried out using various reaction mole ratios of **2a**/**1a**. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (**3a**) was obtained along with 2,6-dichloro-2,4,4,6-tetramethyl-2,4,6-trisilaheptane (**4a**) and others (eq 2). The formation of compound **3a** can be explained by the intermolecular C–Si coupling reaction of the mono-Grignard reagent with **2a**, followed by another C-Si intramolecularly cyclization. Compound **4a** is formed

by two step intermolecular C–Si coupling reactions with **2a**. Others were undesired poly(1,1-dimethyl-1-silapropanes) produced by the ring-opening polymerization of silacyclopropane intermediate.[10] The reaction results obtained at various mole ratio of **2a**/**1a** are summarized in Table 1.



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As shown in Table 1, the yield of **3a** increased from 32% to 62% as the mole ratio of **2a** to **1a** increased to 16 folds from 1 fold. Compound **4a** was observed in trace amount, when high mole ratios between 4 and 16 folds of **2a** to **1a** were used, reflecting that the mono-Grignard reagent of **1a** undergoes the intramolecular cyclization itself, leading to **3a**, much faster than the intermolecular reaction with **2a**, leading to **4a**. When 8 folds or above of **2a** with respect to **1a** was used, the reaction took longer time due to decreasing medium polarity with excess **2** used.

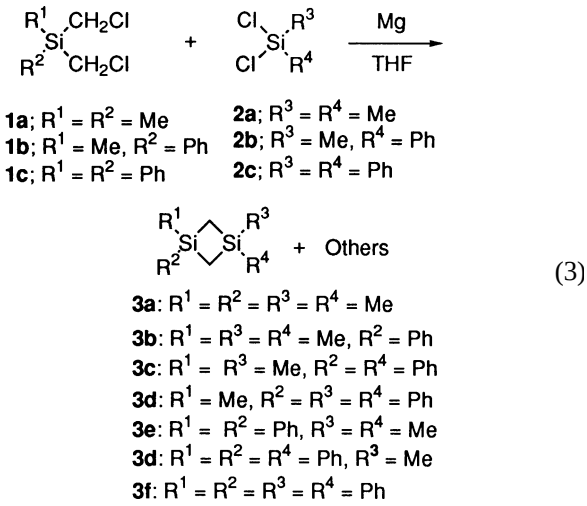
In the case of the 1 : 16 reaction of **1a** and **2a**, the yield of **3a** increased up to 62%. In spite of the result, the product separation from the reaction mixture after general workup was difficult due to cyclic polysiloxane products with the wide range of boiling points (134 °C–high boilers) obtained by the hydrolysis of **2a**.

Preparations of 1,1,3,3-Tetraorgano-1,3-disilacyclobutanes. The Grignard coupling reactions of **1a-c** with dichlorodiorganosilanes ($R^3R^4SiCl_2$): **2a**, $R^1 = R^2 = Me$; **2b,** $R^1 = Me$, $R^2 = Ph$; **2c**, $R^1 = R^2 = Ph$ at the reflux temperature of THF solvent gave 1,1,3,3-tetraorgano-1,3-disilacyclobutanes (eq 3). In such reactions, the mole ratio of **2**/**1** varied with the nature of both reactants in the view of economical production and the separation of product after general workup. The results on the Grignard coupling reaction of **1a-c** and **2a-c** are summarized in Table 2.

Table 1. Product distribution *vs* mole ratios of $Me_2Si(CH_2Cl)_2$ (**1a**) to Me_2SiCl_2 (**2a**)[a]

mole ratio of **2a**/**1a**	reaction time (h)	products		
		3a	**4a**	**5a**
1	3	32	-	7
2	3	45	-	2
4	3	50	trace	3
8[b]	3	53	-	2
	(24)	(56)	trace	4
16[b]	3	57	-	2
	(24)	(62)	trace	trace

[a] The reaction was carried out at the reflux temperature. [b] The yields of products were determined using dodecane as an internal standard by GLC in a 3 h reaction and a 24 h reaction.



(3)

Table 2. Results on Cyclization of $R^1R^2Si(CH_2Cl)_2$ (**1a-c**) with $R^3R^4SiCl_2$ (**2a-c**)[a]

entry no.	reactants			reaction time (h)	product **3** (%)[b]
	1	**2**	**2/1**		
1	**1a**	**2a**	4	6	**3a** (50)
2	**1b**	**2a**	1.2	12	**3b** (46)
3	**1b**	**2b**	4	12	**3c** (42)
4	**1b**	**2c**	1.2	12	**3d** (7)
5	**1c**	**2a**	1.2	12	**3e** (49)
6	**1c**	**2b**	1.2	12	**3d** (48)
7	**1c**	**2c**	1.2	12	**3f** (18)

[a] Reactions were carried out at reflux temperature of THF. [b] Isolated yield.

As shown in Table 2, the cyclized products **3a-f** were obtained in isolated yields ranging from 7% to 50% depending upon the substituents on the silicon atom. Bis(chloromethyl)silanes **1a-c** reacted with methyl-substituted dichlorosilanes **2a, b** to give 1,3-disilacyclobutanes **3a-c**, **e**, **d** in relatively good yields (42–50%), but with dichlorodiphenylsilane (**2c**) to afford 1,3-disilacyclobutanes **3d**, **f** in low yield (7–18%). These results reflect that the low yields of 1,3-disilacyclobutanes in the reaction of bis(chloromethyl)silanes **1a-c** with **1c** are attributable to the steric hindrance[13] of two-phenyl groups on the silicon of **2c** in the Si-C coupling cyclization. In the case of **3c**, two stereoisomers of *cis*- and *tans*- products were obtained in about equal amount.

This study showed that the bis(chloromethyl)diorganosilanes could be utilized as useful starting materials for the preparations of 1,3-disilacyclobutanes having different substituents on each of the two silicon atoms.

Experimental Section

Reagents and Physical Measurements. All operations were carried out in an inert atmosphere. Solvents, tetrahydrofuran (THF), diethyl ether and hexane, were dried over sodium benzophenone ketyl and distilled before use. 2 *M* phenyl magnesium chloride in ethyl ether, 3 *M* methyl magnesium chloride in THF, and other simple chemicals were

purchased from Aldrich Co. and used without further purification. Products were analyzed by gas-liquid chromatography (GLC) using a capillary column (SE-54, 30 m) and a packed column (10% OV-101 on 80-100 mesh Chromosorb W/AW, 1.5 m×1/8 in.) on a Varian 3300 gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector, respectively. The samples for characterization were purified by a preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2 m by 1/8 in. stainless steel column packed with 20% OV-101 on 80-100 mesh Chromosorb P/AW. NMR spectra were recorded on a Varian Gemini 300 spectrometer using chloroform-*d* solvent. Mass spectra were obtained using a Hewlett Packard 5890 Series II gas chromatograph equipped with a Model 5972 mass selective detector. Bis(chloromethyl)dichlorosilane was prepared by photochemical chlorination of dimethyldichlorosilane.[2] Various bis(chloromethyl)diorganosilanes ($R^1R^2Si(CH_2Cl)_2$): **1a** (92%), $R^1 = R^2 = Me$; **1b** (70%), $R^1 = Me$, $R^2 = Ph$; **1c** (95%), $R^1 = R^2 = Ph$ were prepared by the reaction of bis(chloromethyl)diorganosilane[12] with organo Grignard reagents.

Synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (3a).[5a] The reaction of **1a** (2.7 g, 17.2 mmol) with **2a** (8.9 g, 68.8 mmol) and magnesium turning (1.0 g, 41.1 mmol) in THF (30 mL) was carried out for 6 h at reflux temperature. After confirming the disappearance of the Grignard reagent of **1a**, the reaction mixture was cooled down to room temperature, 50 mL of hexane was added. The insoluble salt was filtered off and solvent was removed from reaction mixture. The reaction mixture was fractionally distilled to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**3a**) (1.24 g, 50%) at the temperature of 113 °C. The nonvolatile compounds were treated with 10 mL of water, and 50 mL of ethyl ether was added. The organic suspension layer was separated and vacuum dried to give polymer (0.6 g).

Synthesis of 1,1,3-trimethyl-3-phenyl-1,3-disilacyclobutane (3b).[14] Using the procedure previously described, the reaction of **1b** (3.8 g, 17.2 mmol) with **2a** (2.7 g, 20.6 mmol) and magnesium turning (1.0 g, 41.1 mmol) in THF (30 mL) was carried out for 12 h. The reaction mixture was vacuum (68 °C/1 mmHg) distilled to give **3b** (1.63 g, 46%).

Synthesis of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (3c).[5a,14,15] Using the procedure previously described, the reaction of **1b** (16.3 g, 74.4 mmol) with **2b** (57.3 g, 300.0 mmol) and magnesium turning (7.3 g, 300.3 mmol) in THF (150 mL) was carried out for 12 h. **3c** (8.4 g, 42%) was vacuum distilled out at 124 °C/1 mmHg. **3c** was obtained a mixture (1 : 1) of *cis*- and *trans*-isomers**.**

Synthesis of 1-methyl-1,3,3-triphenyl-1,3-disilacyclobutane (3d). Using the procedure previously described, the reaction of **1b** (3.9 g, 17.8 mmol) with **2c** (5.4 g, 21.4 mmol) and magnesium turning (1.0 g, 41.1.3 mmol) in THF (30 mL) was carried out for 12 h. **3d** (0.4 g, 7%) was vacuum distilled out at 135-144 °C/0.2 mmHg.

As an alternative method, the reaction of **1c** (5.0 g, 17.8 mmol) with **2b** (4.1 g, 21.4 mmol) and magnesium turning (1.0 g, 141.1 mmol) in THF (30 mL) was carried out for 12 h, resulting in **3d** (2.8 g, 48%) and polymer (1.2 g).

Data for **3d**: ^{1}H NMR δ 0.50 (s, 4H, SiCH_2Si), 0.81, 0.87 (each s, 3H, SiCH_3), 7.33-7.37, 7.41-7.43, 7.54-7.60, 7.68-7.70 (m, 15H, phenyl–*H*). ^{13}C NMR δ 1.24 (SiCH_3), 1.53 (SiCH_2Si) 127.90, 129.42, 133.35, 134.28, 137.84 (phenyl–*C*). Mass spectrum, m/z (relative intensity) 330 (6, M^+), 315 (54, $(M\text{-}CH_3)^+$), 253 (33, $(M - C_6H_5)^+$), 252 (100), 240 (25), 239 (97), 237 (35), 195 (21), 105 (27, $PhSi^+$).

Synthesis of 1,1-dimethyl-3,3-diphenyl-1,3-disilacyclobutane (3e).[14] Using the procedure previously described, the reaction of **1c** (5.0 g, 17.8 mmol) with **2a** (2.8 g, 21.4 mmol) and magnesium turning (1.0 g, 41.1 mmol) in THF (30 mL) was carried out for 6 h at reflux temperature. **3e** (2.34 g, 49%) was obtained at temperature of 106 °C/1 mmHg along with high molecular weight products (1.0 g).

Synthesis of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (3f).[5b,14] Using the procedure previously described in the synthesis of **3a**, the reaction of **1c** (5.0 g, 17.8 mmol) with **2c** (5.4 g, 21.4 mmol) and magnesium turning (1.0 g, 41.1 mmol) in THF (30 mL) was carried out for 12 h, resulting in crystal solid **3f** (1.3 g, 18.0%) in hexane solvent and polymer (2.2 g).

Product distributions vs the mole ratio of 2a/1a. The Grignard coupling reactions of **1a** (0.5 g, 3.2 mmol) with **2a** (0.41 g, 3.2 mmol; 0.83 g, 6.4 mmol; 1.65 g, 12.8 mmol; 3.30 g, 25.6 mmol; 6.61 g, 51.2 mmol), magnesium turning (0.33 g, 13.6 mmol), and THF (15 mL) were carried out at the reflux temperature. The progresses of reactions were monitored by a GLC at 1 h time intervals. The yields of products were determined using dodecane as an internal standard by GLC. In the 8 and 16 folds of mole ratio of **2a**/**1a**, the yields of products were obtained in both 3 h reaction and 24 h reaction.

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