Synthesis of Isopropyldichlorosilane by Direct Process

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Direct reaction of elemental silicon with a gaseous mixture of isopropyl chloride (**1**) and hydrogen chloride in the presence of copper catalyst using a stirred bed reactor equipped with a spiral band agitator gave isopropyldichlorosilane having a Si-H bond (**2a**) as a major product and isopropyltrichlorosilane (**2b**) along with chlorosilanes, trichlorosilane and tetrachlorosilane. A process for production of **2a** was maximized using the 1:0.5 mole ratio of **1** to HCl and smaller size of elemental silicon at a reaction temperature of 220 °C. When a reaction was carried out by feeding a gaseous mixture of **1** [12.9 g/h (0.164 mol/h)] and HCl [2.98 g/h (0.082 mol/h)] to a contact mixture of elemental silicon (360 g) and copper (40 g) under the optimum condition for 45 h, **2a** among volatile products kept up about 82 mol % until 35 h and then slowly decreased down 68 mol % in 45 h reaction. Finally **2a** was obtained in 38% isolated yield (based on **1** used) with an 85% consumption of elemental silicon in a 45 h reaction. In addition to **2a**, **2b** was obtained as minor product along with chlorosilanes, trichlorosilane, and tetrachlorosilane. The decomposition of **1** was suppressed and the production of **2a** improved by adding HCl to **1**.

Key Words : Direct process, Isopropyldichlorosilane, Hydrosilane, Elemental silicon, Copper

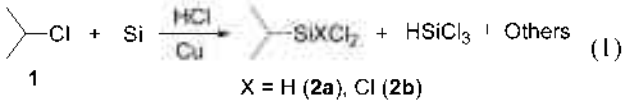
Introduction

Since the preparation method of methylchlorosilanes by directly reacting elemental silicon and methyl chloride in the presence of copper as a catalyst was introduced by Rochow in the early 1940's,[1,2] the direct synthesis is now a basic technology in silicon industry. But the extension of this direct reaction to other long chain organic chlorides such as primary and secondary alkyl chlorides was restricted due to their easy decomposition affording olefin and HCl in the presence of copper at high reaction temperature.[3] Dialkoxysilanes with bulky substituents such as secondary and tertiary alkyl groups are widely used as starting materials for a protecting reagents in organic synthesis, ceramic binder, cross-linker,[4] and electron-donor compounds,[5] for the preparation of polypropylene with high isotacticity using the Zeigler-Natta catalyst. Isopropyl chloride (**1**) is cheap and useful starting material as the simplest secondary alkyl chloride, but its direct reaction has rarely been reported due to the easy decomposition of **1** to propylene and HCl at high temperatures above 280 °C.[3] Direct reaction of **1** with elemental silicon in the presence of a copper catalyst was first reported by Petrov[6] in 1950's. Later, Klebansky[3] and Ono[7] studied the same reaction using a fixed bed reactor at about 280 °C. However the yields of isopropylchlorosilanes such as isopropyldichlorosilane with Si-H (**2a**) and isopropyltrichlorosilane (**2b**) were low below 20%. Isopropylchlorosilanes containing a Si-H bond have are very useful materials and available for the preparation of a variety of organosilicon compounds containing various organic functional groups through hydrosilylation with unsaturated organic compounds.[8] Because their fixed-bed reactor was not effective for dissipating reaction heat, the decomposition of **1** occurred mainly. To solve a problem on the decomposition of **1**, we used a stirred bed reactor that makes it possible to dissipate the heat of reaction more effectively. In addition, hydrogen chloride was used as co-reactant in a reaction with **1** to suppress the decomposition of **1** and to reduce the production of high boilers at the higher temperature.[9-11] Recently we have reported that the hydrogen chloride-incorporating direct reactions of elemental silicon with alkyl chlorides such as (α-chloromethyl)silanes,[9] allyl chloride,[10] dichloromethane,[11a] and chloroform[11b] gave successfully Si-H containing bis(silyl)methanes, allylchlorosilanes, bis(chlorosilyl)methanes, and tris(chlorosilyl)methanes, respectively. This direct reaction was applied for **1**. In particular, this reaction showed that the reactivity of elemental silicon and yields of compound **2a** increased when the smaller particle size of elemental silicon was used. Herein we wish to report the direct synthesis of **2a** from the reaction of elemental silicon with a gaseous mixture of **1** and hydrogen chloride in the presence of copper catalyst using a stirred bed reactor equipped with a spiral band agitator.

Results and Discussion

In the direct synthesis of organochlorosilane, three type reactors such as fixed-bed,[12] stirred-bed,[13] and fluidized-bed[14] have been used, depending on a scale of reaction. Among these systems, the stirred-bed system has advantages over the fixed-system in that the heat of reaction can be dispersed more effectively and the movement of the powders causes fresh surface to be continuously exposed.[9,15] While fluidized-bed system is suitable for a direct synthetic process in a large scale.[14] Thus, stirred-bed reactor was applied for the direct synthesis of **2a**. A contact mixture of

elemental silicon and copper catalyst prepared by a known method[6] was reacted with a gaseous mixture of **1** and hydrogen chloride in a stirred-bed reactor equipped with a spiral band. In a reaction, **2a** was obtained as major product along with **2b** and chlorosilanes, trichlorosilane and a trace of tetrachlorosilane (eq 1). In order to find the optimum condition for the preparation of **2a**, reaction was carried out at various conditions such as reaction temperature, the mixing ratio of HCl/**1**, and elemental silicon sizes.



(1)

Effect of Reaction Temperature. Direct reaction of elemental silicon with a 1:0.5 gaseous mixture of **1** to hydrogen chloride was carried out at various reaction temperatures from 220 °C to 300 °C. Reaction mixture was fractionally distilled to give $HSiCl_3$, **2a**, and **2b**. The amounts and compositions of products collected from the direct reaction of **1** at various reaction temperatures are summarized in Table 1.

As shown in Table 1, the total weight amount of products received and percentage of **2a** were the highest at a 220 °C (entry no. 2) of reaction temperature among reactions carried out at temperatures ranged from 200 °C to 300 °C. In the reaction, the yield of **2a** was maximized to 45% at 220 °C and went down 18% at 200 °C (entry no. 1) and 22% at 300 °C (entry no. 4), respectively. This reaction temperature is very lower when compared with the direct reaction of primary alkyl chlorides.[1,2]

Mixing Ratio of the Reactants. In order to suppress the decomposition of **1** leading to propylene and hydrogen chloride,[9-11] hydrogen chloride-incorporated direct reaction of **1** with elemental silicon was carried out at 220 °C. Results obtained from the direct reaction using various mixing ratios of hydrogen chloride/**1** ranging from 0 to 1 in the presence of copper catalyst at 220 °C for 4 h are given in Table 2.

Table 1. Effect of Reaction Temperature on the Direct Reaction of **1**[a]

entry no.	reaction temp. (°C)	products (g)	**2** (wt %)	yields (%)[b] **2a**	**2b**	$HSiCl_3$ (wt %)	others (wt %)
1	200	11	73	18	1	12	15
2	220	24	84	45	2	13	3
3	260	18	81	30	2	14	5
4	300	15	73	22	3	16	11

[a]21.5 g of **1** was used for 4 h. Catalyst: Cu (10 wt %). Elemental silicon size: 45-75 μm. Mol ratio of hydrogen chloride to **1** = 1:0.5. [b]Isolated yields.

Table 2. Mixing Ratio of the Reactants[a]

entry no.	mole ratio (HCl/1)	products (g)	**2** (wt %)	yield (%)[b] **2a**	**2b**	$HSiCl_3$ (wt %)	others (wt %)
5	0	17	88	32	2	4	8
2	0.5	24	84	45	2	13	3
6	1.0	27	70	41	2	27	3

[a]21.5 g of **1** was used for 4 h. Catalyst: Cu (10 wt %). Elemental silicon size: 45-75 μm. Reaction temperature: 220 °C. [b]Isolated yelds

As shown in Table 1, compound **2a** was obtained as major product in the direct reaction of **1** without hydrogen chloride and the yield was not bad. This indicates that hydrogen chloride formed from the decomposition of some of reactant **1** was involved in the formation of **2a**.[7] In HCl-incorporating direct reaction of **1**, the yield of **2a** increased to 45% from 32% as the ratio of hydrogen chloride/**1** increased from 0 to 1, indicating that the decomposition of **1** to hydrogen chloride was suppressed. Similar results have been observed in other system.[7,9,10] In viewpoint of economical process, yield of **2a** was good when a 1:0.5 ratio of **1** and hydrogen chloride was used.

Silicon Particle Size. Influence of size and distribution of particles of elemental silicon on the direct reaction of **1** was studied using various particle sizes ranging from 45 to 150 μm. The results obtained from the reactions using fine and narrow sized particles of elemental silicon are summarized in Table 3.

As shown in Table 3, when the direct synthesis was carried out using elemental silicon above 75 μm (entry no. 7) and the ranged of 45-150 μm (entry no. 8), **2a** was obtained in better yield at higher temperature above 300 °C. But the reaction temperature decreased down 220 °C and the yield of **2a** was even better using below 75 μm of particle sizes (entry no. 2). It is interesting to note that direct reaction of **1** occurred effectively at lower temperature of 220 °C, which is a 100 °C lower than that for the direct reaction of methyl chloride.[2] This results showed that smaller particle sizes of elemental silicon has more advantageous in the production of **2a** and the reduction of the carbon deposition on the surface of contact mixture.[3]

As a preparative method, the direct reaction of elemental silicon with a 1:0.5 gaseous mixture of **1** to HCl was continuously carried out at 220 °C for 45 h. All reaction

Table 3. Effect of Metal Size on the Direct Reaction of **1**[a]

entry no.	metal size (μm)	reaction temp. (°C)	products (g)	**2** (wt %)	yields (%)[b] **2a**	**2b**	low boilers[d] (wt %)	others (wt %)
2	45-75	220	24	85	45	2	13	2
7	75-104	300	20	89	42	2	6	5
8	45-150[c]	320	43	12	9	–	84	4

[a]21.5 g of **1** was used for 4 h. Catalyst: Cu (10 wt %), HCl/**1** = 10.5. [b]Isolated yelds. [c]Elemental silicon sizes consisting of 45-75 μm (17%), 75-104 μm (34%), and 104-150 μm (49%). [d]A 24: 1 mixture of $HSiCl_3$ to $SiCl_4$.

products were collected after the analysis of each of reaction mixture received in every 100 min. In the reaction, **2a** among volatile products of each container received kept up about 82 mol % until 35 h and then slowly decreased down 68% in 45 h reaction. After 45 h reaction, **2a** was obtained in 38% isolated yield (based on **1** used) with an 85% consumption of elemental silicon. In addition to **2a**, **2b**, trichlorosilane, and tetrachlorosilane were formed as by-products in low yields, respectively.

Experimental Section

Reagents and Physical Measurements. **1** was purchased from Aeros Organics and dried over calcium chloride under dry nitrogen and distilled before use. Anhydrous hydrogen chloride (99.999%) was purchased from Matheson Co. and used without further purification. Copper powder was purchased from Alcan Metal Powders (Elizabeth, NJ). Elemental silicon OSI-5-4855 (45-75 μm) was purchased from Elkem Silicon (Oslo, Norway). Products were purified by fractional distillation and analyzed by analytical GLC over a 1.5 m by 1/8 in. O.D. stainless steel column packed with packing material (10% OV-101 or SE-30 on 80-100 mesh chromosorb W/AW) using a Varian 3300 gas chromatograph, equipped with a thermal conductivity detector. Mass spectra were obtained from Hewlett-Packard 6890 Series gas chromatograph equipped with Model 5973 mass selective detector.

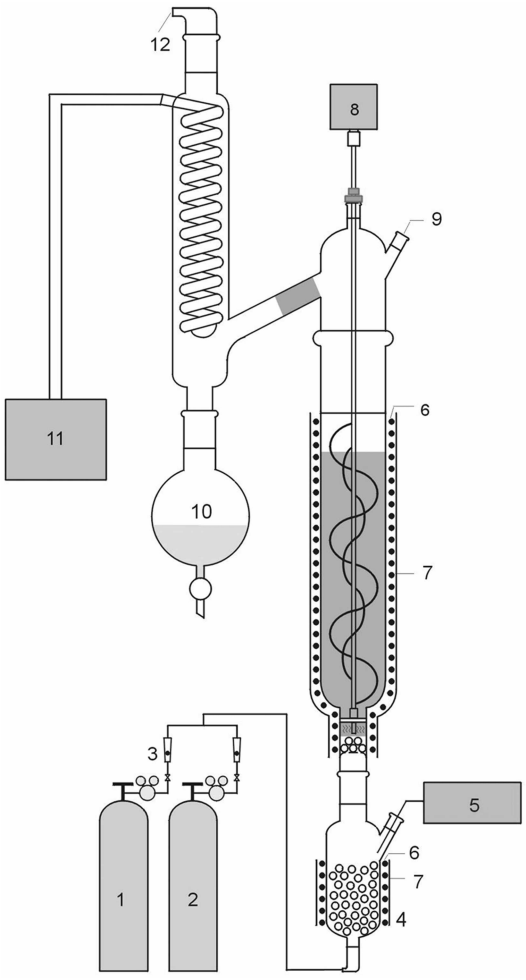


Figure 1. Reactor for the direct synthesis of isopropyldichlorosilane.

Reactor. The reactor was made of a Pyrex glass, 50 mm inner diameter and 38 mm length, with an electrical heating wire coiled outside the reactor. A spiral band agitator was made of 1/4 inch stainless steel tube which was doubly coiled with a 4 mm stainless steel tube. Gas flow rates were controlled by a Matheson 603 flow meter. Coolant (−23 °C) was circulated to the condenser for collecting products (Figure 1).[9]

General Procedure for the Direct Reaction of 1. A mixture of elemental silicon (360 g, 45-75 μm) and 40.0 g of copper catalyst was placed in a Pyrex glass tube reactor, 50 mm inner diameter and 400 mm length, with an electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was dried at 300 °C for 4 h while a dry nitrogen flush was maintained. Then the temperature was raised up to 350 °C and methyl chloride was introduced at the rate of 15.2 g/h to activate the contact mixture for 4 h. After removal of products formed (such as dimethyldichlorosilane and methyltrichlorosilane) during the activation process, the temperature was adjusted to 220 °C and then **1** was introduced using a syringe pump into the evaporator attached at the bottom of the reactor at a rate of 12.9 g/h (0.164 mol/h). At the same time gaseous hydrogen chloride was introduced at a rate of 2.98 g/h (0.082 mol/h) with the 1: 0.5 mole ratio of **1** to hydrogen chloride. All reaction products were collected after the analysis of each of reaction mixture received at every 100 min. In the reaction, **2a** among volatile products of each container received kept up about 82 mol % until 35 h and then slowly decreased down 68% in 45 h reaction. After 45 h of reaction, 569 g of the products, collected in the receiver cooled –20 °C, was distilled at atmospheric pressure to give trichlorosilane (85 g, 32 °C), tetrachlorosilane (3 g, 57 °C), **2a** (434 g, 92-3 °C), and **2b** (13 g, 115-6 °C), respectively. The residue was bulb to bulb distilled at 50-250 °C/0.5 mmHg to give 16 g of a mixture of high boiling products.

Using the same procedure as above, we studied the optimum reaction conditions such as temperature, the mixing ratio of hydrogen chloride to **1**, and size effect of metallic silicon for the direct synthesis of **2a**. Data for **2a**: δ 1.15-7 (d, J = 6.0 Hz, 6H, C*H*$_3$), 1.34-1.39 (m, 1H, C*H*), 5.39 (s, 1H, Si*H*); ^{13}C NMR δ 15.6 (*C*H$_3$), 18.68 (Si-*C*H); mass spectrum (70 eV, EI), m/z (rel intensity) 144 (34, $(M+2)^+$), 142 (50, M^+), 115 (22), 113 (33), 101 (67), 99 (98), 65 (49), 63 (100). Data for **2b**: ^{1}H NMR δ 1.18-20 (d, J = 7.2 Hz, 6H, C*H*$_3$), 1.48-1.58 (m, 1H, C*H*); ^{13}C NMR δ 15.7 (*C*H$_3$), 22.63 (Si-*C*H); mass spectrum (70 eV, EI), m/z (rel intensity) 176

(4, M^+), 163 (23), 161 (23), 144 (13), 142 (69), 140 (100), 133 (69), 125 (17), 112 (12), 98 (10), 63 (21).

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