

Dephenylation of Decaphenylcyclopentasilane with HCl Catalyzed by Aluminum Chloride: Facile Synthetic Route to Cyclopentasilane

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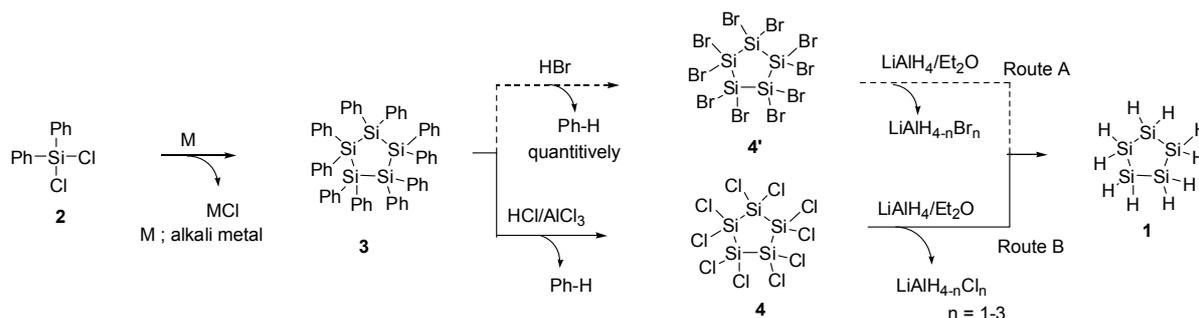
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Hydrosilanes are useful precursors for fabrication of electronic devices such as silicon thin-film transistors.^{1-3,4a} It is now well known that especially monosilane is widely utilized as good precursors in electron industry but their thermal depositions to polysilicon require high temperature and vacuum processes.¹ Recently much attention has been paid to alternative solution processes such as spin coating and inkjet printings, which are very promising to significantly improve fabrication without vacuum process on a large scale.² For this solution process, requirements of precursors applicable to solution process are relatively low volatile and soluble in common organic solvents. There are some candidates of liquid phase hydrogenated silicon compounds are either of the cyclic polysilanes forms such as cyclopentasilane³ and cyclohexasilane^{4a} or linear-chain. Cyclopentasilane (**1**), which is a discrete molecule as a liquid phase and soluble in various organic solvents, is the best precursor from the viewpoint of its synthesis and purification,³ many patents on its application for solution processes have been filed.⁵ Generally compound **1** has been prepared from three step reactions^{2,3} starting from diphenyldichlorosilane (**2**): 1) dechlorinative Si-Si coupling reaction of **2** with alkali metal giving decaphenylcyclopentasilane (**3**),⁶ 2) dephenylative bromination of **3** with HBr affording decabromocyclopentasilane (**4'**), 3) then the reduction of **4'** with lithium aluminum hydride leading to **1** (Route A in Scheme 1).³ In this synthetic route, **3** reacted with hydrogen bromide in benzene solvent in a bomb tube to afford quantitatively perbrominated pentasilane **4'**.³ Especially hydrogen bromide has been widely used as an agent for dearylyative bromination of phenylsilane affording the high yield synthesis of bromosilane.³ While the dearylyative chlorination reaction

using hydrogen chloride requires a strong Lewis acid catalyst such aluminum chloride as a catalyst (Route B in Scheme 1). In the reduction steps of both routes, excess amount of lithium aluminum hydride is required and the lot of complexes of lithium aluminum halides (LiAlH_4X_n , X = Br, Cl) are formed as byproducts. In the reduction reaction, the conversion of **4'** to **1** can be reduced to 16 wt% in viewpoint of molecular weight change, indicating that an 84% of weight of **4'** used can be converted to byproducts, lithium aluminum bromide complexes which are soluble in organic ethers and partially in nonpolar solvent (benzene). Such soluble aluminum halide can also catalyze the decomposition reaction in a step of vacuum fractional distillation of **1**. While lithium aluminum chloride is less soluble in organic solvent than lithium aluminum bromide due to its higher ionic character of metal chloride. We have focused on a development of facile synthetic route B to **1** including a dephenylative chlorination of **3** using hydrogen chloride in the presence of aluminum chloride instead of hydrogen bromide (Route A).

Based on early literature,^{6,7} the reaction of dichlorosilane **2** with lithium in THF solvent at room temperature was carried out. A mixture of cyclic polysilanes was formed as major products along with linear polysilanes. Decaphenylcyclopentasilane **3** could be obtained as colorless powders in 49% yield along with octaphenylcyclotetrasilane (28%) by a recrystallization from a mixed benzene-hexane solution of cyclic polysilane compounds. The dephenylative chlorination of **3** was carried out with bubbling of hydrogen chloride gas in the presence of catalytic amount of aluminum chloride.⁸ The progress of the reaction was monitored at intervals of 30 min by the analysis of ¹H NMR data. In ¹H NMR data, the intensity



Scheme 1. Synthetic Route to cyclopentasilane from Ph_2SiCl_2 .

of resonances of phenyl groups on the silicon with a multiplet splitting pattern at 6.89 - 7.64 ppm were disappeared as the reaction progressed. The reaction was stopped when the resonances of phenyl groups on the silicon were disappeared. In the last step reaction, excess amount of lithium aluminum hydride was used. The 1 : 6 mol ratio reaction of perchlorinated polysilane **4** with lithium aluminum hydride in THF at room temperature for 2 h gave quantitatively **1** and a mixture of lithium aluminum chloride complexes would be formed about 79 wt% (based on both reactants used) as byproduct. The loss of **1** occurred in the isolation step from the complexes of lithium aluminum chloride byproducts. Total yield of **1** starting from **3** was 83% (Route B). When both reduction reactions of **4'** and **4** with LiAlH₄ are compared, 70 wt% of **4** used in the reaction was converted to lithium aluminum chloride complexes while 84 wt% of **4'** to lithium aluminum bromide complexes as byproducts based on their molecular weight changes, suggesting that the amount of byproducts from the reduction of **4'** is much higher than that of **4**. That is a reason why the route B to **1** (83%) is better than the route A (75%)^{3b} in a view to the high purity synthesis of a discrete molecule suitable for electronic devices.

In summary, we were successfully developed an alternative synthetic route **B** for the synthesis of **1** applicable to the solution processing of silicon thin-film transistors (TFTs): dephenylative chlorination reaction of **3** with anhydrous HCl in the presence of aluminum chloride at room temperature gave quantitatively **4**, which gave **1** in 83% yield through a hydrogenation with LiAlH₄ in diethyl ether and a vacuum fractional distillation.

Experimental Section

Reagents and Physical Measurements. All operations were carried out in an inert gas atmosphere. Solvents, tetrahydrofuran (THF) and benzene, were dried by sodium benzophenone ketyl and distilled before use. Anhydrous hydrogen chloride (99.999%) was purchased from a Solktronic chemical and used without further purification. Other simple chemicals were purchased from Aldrich Chemical Co. and used without further purification. The product was analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80 - 100 mesh chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ¹H), Bruker AMX 500 (FT, 500 MHz, ¹H; 125 MHz, ¹³C), or a Varian Gem 300 (FT, 300 MHz, ¹H; 75 MHz, ¹³C) spectrometer in CDCl₃ or C₆D₆ solvent. Mass Spectrometer (JEOL, Japan) at electron energy of 70 eV.

General Si-Si Coupling Reaction of 2.^{6,7} To a stirring lithium metal (25.0 g, 3.6 mol) in THF (800 mL) at ice-water temperature for 2 h was added dichlorodiphenylsilane (455.0 g, 1.8 mol). The reaction initiated within a few min, as indicated by the evolution of heat and reaction solution was changed to red-brown. After the addition was completed, the resulting reaction mixture was stirred for another 12 h at room temperature. Then one mL of water was added to quench the

active species. The insoluble material was removed by filtration and THF solvent was removed to give white powders. This white powder was dissolved in benzene (500 mL) and the insoluble powders were extracted four times with cold benzene (60 mL × 5) to leave 97 g. From the benzene soluble compounds, **2** (155 g, 47%) and octaphenylcyclotetrasilane (92 g, 28%) were isolated by recrystallization of its benzene-hexane mixed solvent system.

General Procedure for the Dephenylative Chlorination of 3 and Its Reduction. Into a stirring solution of **3** (24.1 g, 0.026 mol), dried benzene (300 mL), and aluminum chloride (0.34 g, 0.0026 mol) was bubbled hydrogen gas at a rate of 0.15 g/min (0.1 L/min) at room temperature for 2 h. The progress of reaction was monitored at intervals of 30 min. by the analysis of ¹H NMR data. When the reaction was completed, the resonances of phenyl groups on the silicon were disappeared at the down field of 6.89 - 7.64 ppm (in CDCl₃). Then, the reaction mixture was added to a stirring suspension of diethyl ether (500 mL) and lithium aluminum hydride (6.22 g, 0.16 mol) at ice-water temperature for 1 h. The reaction mixture was stirred at room temperature for another 2 h and concentrated by evaporation of solvent under a reduced pressure of 30 torr. When the remaining reaction mixture was about 80 - 90 mL, *n*-pentane (400 mL) was added to extract the product **1** from lithium aluminum chloride complexes. Then the insoluble solids were filtered out and washed four times with cold *n*-pentane (30 mL × 4). The filtrate was concentrated under reduced pressure, some precipitation occurred, and filtered off again. The same purification cycles were repeated more 2 times until insoluble solid was not precipitated and finally vacuum-fractional distilled at 0.05 torr to give product **1** (3.3 g, 83%). Compound **1** was identified with comparing with the data of literature.³

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