

Table 2. Selective Reduction of Aldehyde Groups in the presence of Keto and Other Functional Groups with $\text{Ipc}_2\text{O}^t\text{Bu}$ in Pentane at 25 $^\circ$

Starting mixture	Time (h)	Ratio of reduction products ^b
Butanal/Cyclohexanone	1	100 : 0
Hexanal/Cyclohexanone	6	100 : 0
Hexanal/2-Heptanone	6	100 : 0
Hexanal/Acetophenone	6	100 : 0
Hexanal/Benzophenone	6	100 : 0
Benzaldehyde/Hexanal	6	60 : 40
Benzaldehyde/Cyclohexanone	6	100 : 0
Benzaldehyde/2-Heptanone	6	100 : 0
<i>p</i> -Anisaldehyde/Cyclohexanone	6	>99.9 : trace
Hexanal/Hexanoyl chloride	6	100 : 0
Hexanal/Benzoyl chloride	6	100 : 0
Hexanal/1,2-Butylene oxide	6	100 : 0

^aReaction mixture were ca. 1 M in substrates. One equivalent of reagent was utilized for competitive reduction of equimolar mixture of two carbonyl compounds. ^bNormalized ratio determined by GLC with appropriate internal standard; the total yields of product alcohols were $\geq 99.9\%$.

tained by GC analysis of the reaction mixture with internal standard are summarized in Table 2.

Both aliphatic and aromatic aldehydes examined are selectively reduced in the presence of simple ketones: hexanal is selectively reduced in the presence of even cyclohexanone. Likewise, benzaldehyde can be selectively reduced in the presence of cyclohexanone. Even more important is the chemoselective discrimination between hexanal and acid chloride. Furthermore, epoxides are inert to the reagent. Consequently, the reagent permits the selective reduction of aldehyde groups in the presence of nearly all other functional groups. Although Ipc_2BOH has proven to be the most excellent reagent in its ability to discriminate between an aldehyde and a ketone, the reduction rate is quite slow: the reagent requires a 24 h reaction at 25 $^\circ$ for completion.¹ Consequently, a remarkable inertness of $\text{Ipc}_2\text{BO}^t\text{Bu}$ toward most of the functional groups, coupled with a superior selectivity (100%) and a high reactivity (6 h at 25 $^\circ$) in the reduction of aldehydes provide an extremely useful method for such selective reduction.

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Direct Synthesis of α,α -Bis(silyl)toluenes

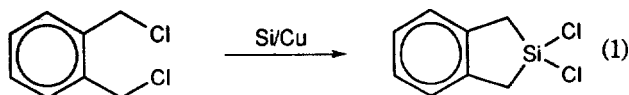
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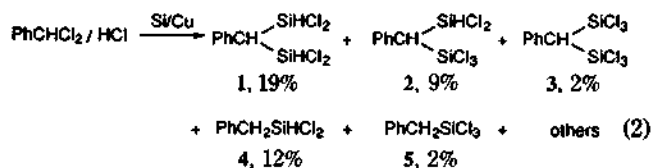
Since the direct synthesis of methylchlorosilanes from elemental silicon and methyl chloride catalyzed by copper was invented by Rochow in 1940's,¹ direct reactions of metallic silicon with various alkyl chlorides have been studied extensively.² However the direct reaction of benzyl chloride has not been reported yet, because benzyl chloride decomposes rapidly when contact with Si-Cu contact mass at temperature above 150 $^\circ\text{C}$.³ We recently reported the direct synthesis of 2,2-dichloro-2-silaindan by reacting α,α' -dichloro-*o*-xylene with elemental silicon (eq. 1).⁴ It was first example that benzylic chloride was used in the direct synthesis. We also found that hydrogen chloride addition to organic chlorides in the direct synthesis suppressed the decomposition of starting compounds and gave the Si-H containing silane products mainly.

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We wish to report herein the preparation of Si-H containing α,α -bis(silyl)toluenes by directly reacting elemental silicon with a mixture of α,α -dichlorotoluene and hydrogen chloride in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at carefully controlled temperatures between 280 and 360 °C.

The direct reaction was carried out as shown in the following typical example using the same reactor as described elsewhere.^{5a} A mixture of 90.0 g of elemental silicon (100-325 mesh) and 10.0 g of copper was placed in a reactor made of Pyrex® glass tube (25 mm inner diameter and 400 mm length) with an electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was flushed at 350 °C for 2 h with a dried nitrogen. At this point, methyl chloride was introduced at the rate of 60 mL/min to activate the contact mixture for 4 h. After removing the methylchlorosilanes formed during activation, 0.50 g of cadmium powder was added at 30 °C, the inside temperature of the contact mixture was maintained at 320 °C during 1 h. Then the temperature was readjusted to the desired reaction temperature, e.g. 320 °C, and α,α -dichlorotoluene was added using a syringe pump into the evaporator attached at the bottom of the reactor at the rate of 6.62 mL/h. Simultaneously, hydrogen chloride flow rate was set to 115 mL/min by using Matheson 600 rotameter. Nitrogen flow was set to 60 mL/min to remove the products out of the reactor better. The products were collected in the receiver at the top of the reactor. From the 49.6 g (308 mmol) of the α,α -dichlorotoluene, 17.4 g (19% yield) of 1,1,3,3-tetrachloro-2-phenyl-1,3-disilapropane, **1**,⁶ 9.4 g (9% yield) of 1,1,1,3,3-pentachloro-2-phenyl-1,3-disilapropane, **2**,⁷ 2.0 g (2% yield) of 1,1,1,3,3,3-hexachloro-2-phenyl-1,3-disilapropane, **3**,⁸ 7.0 g (12% yield) of benzylchlorosilane, **4**,⁹ and 2.0 g (2% yield) of benzyltrichlorosilane, **5**¹⁰ were obtained along with 0.9 g of benzene, 1.0 g of toluene, 0.4 g of diphenylmethane, 0.6 g of 1,2-diphenylethane, and 2.0 g of *trans*-stilbene. The yields were calculated on the basis of starting α,α -dichlorotoluene.



The product, **1** was presumably derived from the reaction in which 1 mol of α,α -dichlorotoluene and 2 mol of hydrogen chloride reacted with the silicon atom simultaneously. The product, **2** was obtained from the reaction in which 1 mol of α,α -dichlorotoluene and 1 mol of hydrogen chloride reacted with the silicon atom followed by chlorine abstraction. The product, **3** was similarly derived from the reaction of 1 mol of α,α -dichlorotoluene and 2 mol of chlorine with the silicon atom. The products, **4** and **5** were presumably produced from benzyl chloride which derived from the reduction of α,α -dichlorotoluene by hydrogen chloride in the contact mixture.

In order to optimize the reaction temperature for the di-

Table 1. Effect of Reaction Temperature on the Direct Synthesis^a

Entry no.	Reaction temp. (°C)	Amount of product (g)	Products composition (wt %)				
			1	2	3	4	5
1	280	7.3	3.1	4.9	5.0	3.4	2.4
2	300	4.9	25.0	25.5	6.9	7.9	2.3
3	320	10.6	28.8	17.5	2.9	12.3	3.1
4	340	10.5	27.0	16.4	2.5	10.5	2.1
5	360	11.0	19.8	15.3	3.9	6.9	2.2

^aCatalyst/co-catalyst : 10% Cu/0.5% Cd. Mole ratio of α,α -dichlorotoluene/hydrogen chloride : 1/6. α,α -Dichlorotoluene, 8.3 g, was used during 1 h of reaction time.

Table 2. Effect of Mole Ratio on the Direct Synthesis^a

Entry no.	Mole ratio ^b	Amount of product (g)	Products composition (wt %)				
			1	2	3	4	5
6	1 : 4	6.5	11.5	21.5	12.7	9.3	7.2
3	1 : 6	10.6	28.8	17.5	2.9	12.3	3.1
7	1 : 9	16.6	14.7	8.6	2.1	7.2	1.7

^aCatalyst/co-catalyst : 10% Cu/0.5% Cd. Reaction temperature : 320 °C. α,α -Dichlorotoluene, 8.3 g, was used during 1 h of reaction time. ^b α,α -Dichlorotoluene : hydrogen chloride.

rect reaction, the reactions were carried out at the various reaction temperatures ranging from 280 to 360 °C and product distributions are given in Table 1. In this study, 0.5% of cadmium was employed in all experiments, because it was known as a best promoter for the direct synthesis of Si-H containing chlorosilanes.⁵

Although several byproducts were also obtained together from the reaction, the benzal and benzyl containing chlorosilanes were only included in the table for simplicity. The low boiling rest were almost about 5 : 1 mixture of trichlorosilane and tetrachlorosilane that produced from the reaction of hydrogen chloride and elemental silicon. As shown in the Table 1, the starting α,α -dichlorotoluene was not detected in the products throughout the reaction temperatures except 280 °C, indicating that the reaction temperature 280 °C was too low for the reaction. For all cases, **1** was obtained as the major product except 280 °C. The total amount of products and selectivity for **1** gradually increased as the temperature increased up to 320 °C. However, beyond 320 °C the amount of products and the selectivity decreased again, suggesting higher decomposition of α,α -dichlorotoluene at higher reaction temperatures.

To study the effect of hydrogen chloride addition, the direct reaction was carried out using various mixing ratios of α,α -dichlorotoluene and hydrogen chloride at 320 °C. The product distributions obtained from the direct reaction are given in Table 2.

As shown in Table 2, the total amount of products increases with increase of hydrogen chloride addition because the large amount of trichlorosilane and tetrachlorosilane were produced from the reaction between silicon and hydro-

gen chloride.¹¹ The yield of **1** based on α,α -dichlorotoluene consumption also increases as hydrogen chloride increases. This result suggests that a higher mixing ratio of hydrogen chloride content suppress the decomposition of α,α -dichlorotoluene better. In the case of mole ratio of reactants higher than 1:6, however, about same amounts of products (**1-5**) were obtained.

In summary, we have shown that the direct synthesis of α,α -bis(silyl)toluenes successfully by reacting elemental silicon with a mixture of α,α -dichlorotoluene and hydrogen chloride in the presence of copper catalyst.

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6. Characterization data for 1,1,1,3,3-tetrachloro-2-phenyl-1,3-disilapropane (**1**): ¹H NMR (CDCl₃) δ 2.80 (t, $J=1.9$ Hz, 1H, CH), 5.71 (d, $J=1.9$ Hz, 2H, Si-H), 7.21-7.42 (m, 5H, ArH); ¹³C NMR (CDCl₃) δ 35.39 (CH), 127.22, 129.40, 129.63, 131.07 (Ar). HRMS (m/e): calcd for C₇H₄Cl₄Si₂ (M⁺), 287.8919; found, 287.8914.
7. Characterization data for 1,1,1,3,3-pentachloro-2-phenyl-1,3-disilapropane (**2**): ¹H NMR (CDCl₃) δ 2.98 (d, $J=1.9$ Hz, 1H, CH), 5.74 (d, $J=1.9$ Hz, 1H, Si-H), 7.20-7.43 (m, 5H, ArH); ¹³C NMR (CDCl₃) δ 38.98 (CH), 127.50, 129.53, 129.77, 130.58 (Ar). HRMS (m/e): calcd for C₇H₃Cl₅Si₂ (M⁺), 321.8529; found, 321.8539.
8. Characterization data for 1,1,1,3,3,3-hexachloro-2-phenyl-1,3-disilapropane (**3**): ¹H NMR (CDCl₃) δ 3.17 (s, 1H, CH), 7.26-7.42 (m, 5H, ArH); ¹³C NMR (CDCl₃) δ 42.25 (CH), 127.76, 129.36, 130.15, 130.32 (Ar). HRMS (m/e): calcd for C₇H₂Cl₆Si₂ (M⁺), 355.8139; found, 355.8177.
9. Benzylidichlorosilane (**4**): ¹H NMR (CDCl₃) δ 2.76 (d, $J=2.0$ Hz, 2H, CH₂), 5.54 (t, $J=2.0$ Hz, 1H, Si-H), 7.18-7.37 (m, 5H, ArH).
10. Benzyltrichlorosilane (**5**): ¹H NMR (CDCl₃) δ 2.92 (s, 2H, CH₂), 7.29-7.36 (m, 5H, ArH).
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Diels-Alder Reactions of α -Phenylthio- o -Quinodimethanes

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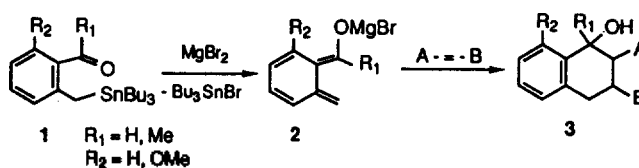
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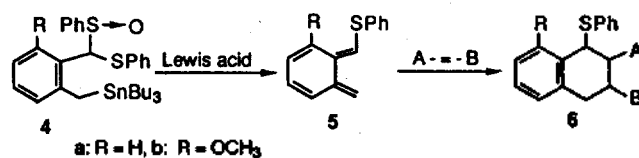
The generation and synthetic utility of o -quinodimethanes as the diene partner in Diels-Alder cycloaddition reactions is well documented.¹ In the previous report,² we found that the reactions of stannyl aldehydes and ketones **1** with anhydrous MgBr₂ at 0 °C in CH₂Cl₂ led to α -oxy- o -quinodimethanes **2**, which could be trapped as Diels-Alder adducts in good yields (Scheme 1).

As an extension of this study, we now wish to report a new and mild method for the generation of α -phenylthio- o -quinodimethanes **5** by the Lewis-acid promoted internal carbon-tin bond cleavage reaction of dithioacetal S-oxides **4** (Scheme 2). The method utilizes the potential of the C-Sn σ bond as a latent carbanionic nucleophile³ and the sensitivity of sulfoxides as a leaving group in the presence of Lewis acids.⁴ It is noteworthy that despite the well-known activating and regiodirecting effects of the sulfur substituents on diene in Diels-Alder reaction,⁵ no report has yet been described concerning the generation and cycloadditions of o -quinodimethanes bearing the sulfur substituents at the α position.

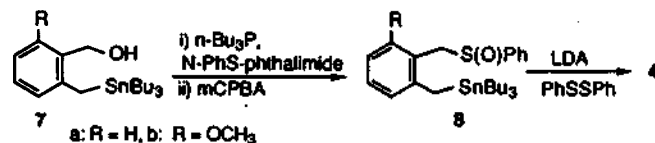
The requisite precursors **4** employed in the present study were easily prepared from the known stannyl alcohols **7**^{2,3} in three steps (Scheme 3). Reaction of **7** with *n*-Bu₃P and *N*-(phenylthio)phthalimide in benzene at room temperature⁶ afforded their corresponding sulfides, which were subjected to *m*CPBA oxidation (1 equiv, -78°--50 °C/CH₂Cl₂/2 h) to give sulfoxides **8** in 70-75% overall yields. Sequential treat-



Scheme 1.



Scheme 2.



Scheme 3.