

**Figure 3.** Plots of CV peak current vs.  $v^{1/2}$  at the glassy carbon electrode for the reduction of the  $\text{SOCl}_2$  solution containing a) 0 and b) 0.61 mM Fe(II)-TSBP.

of additive is described by a curve with a clearly defined current maximum  $i_p$  at the potential  $E_p$  of about 2.684 V vs. Li. The current drop at less positive potentials seems to be due to passivation of the electrode by lithium chloride<sup>19</sup>. Introduction of 0.61 mM Fe(II)-TSBP complex into the net  $\text{SOCl}_2$  solution (13.71 mole/l) leads to an increase of the maximum peak current  $i_p$ . In the presence of Fe(II)-TSBP, the catalytic effect is clearly seen as shown by the positive shift in the potential for thionyl chloride reduction and an increase in cyclic voltammetric peak current. Enhancement in power density of 130% is noted for the glassy carbon electrode. Figure 2 shows voltammograms in the presence of 0.61 mM Fe(II)-TSBP at different scanning rates  $v$ . The dependence of  $i_p$  on  $(v)^{1/2}$  for solutions without and with Fe(II)-TSBP addition (Figure 3) are both linear, but differ in slope. In this result, significant improvement in cell performance is noted in terms of exchange rate constant of up to 10 times. Most of the enhancement originates from improvements in apparent diffusion coefficient and exchange rate constant in thionyl chloride solution containing catalyst.

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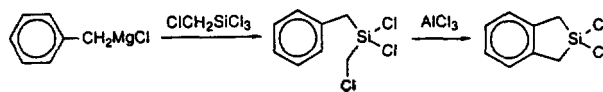
## Direct Synthesis of 2,2-Dichloro-2-silaindan

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Since the direct synthesis of chloromethylsilanes from metallic silicon and methyl chloride at high temperature around 300°C was discovered by Rochow,<sup>1</sup> direct reactions of metallic silicon with various alkyl chlorides have been studied extensively.<sup>2</sup> However, the direct reaction of benzyl chloride with silicon has not been reported yet, because benzyl chloride decomposes rapidly when contacted with Si-Cu contact mixtures at temperature above 150°C.<sup>3</sup> We have attempted the direct reaction of metallic silicon with  $\alpha, \alpha'$ -dichloro-*o*-xylene having two benzylic chlorides within the molecule. 2,2-Dichloro-2-silaindan is expected to be prepared directly from metallic silicon and  $\alpha, \alpha'$ -dichloro-*o*-xylene. Alkyl-2-silaindanes are known to undergo a ring opening polymerization and the resulting polymers have high melting temperature and thermal stability.<sup>4</sup> Therefore, 2,2-dichloro-2-silaindan is a strong candidate as a starting material for the ring opening polymerization. Until now 2,2-dichloro-2-silaindan (I) has only been prepared in multiple steps using various techniques such as Grignard and Friedel-Crafts reactions as following.<sup>5</sup>



I

We wish to report here in the first preparation of I by directly reacting metallic silicon with  $\alpha, \alpha'$ -dichloro-*o*-xylene

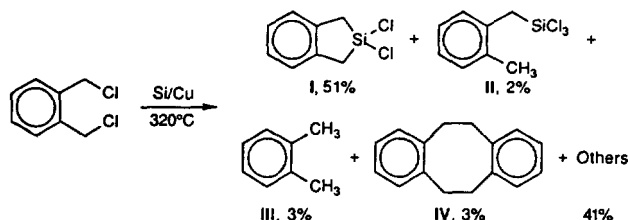
**Table 1.** The Reaction Temperature and Product Compositions\*

Temp. (°C)	Tot. amount of products (g)**	Product Compositions (%)***			
		I	II	III	IV
260	8.99	69.1	2.6	2.3	4.1
280	9.40	70.9	2.8	2.5	3.6
300	9.21	71.5	2.8	3.4	3.9
320	8.92	69.9	2.9	3.5	4.3

\*10.08 g of  $\alpha,\alpha'$ -Dichloro-*o*-xylene in toluene solution (47.65 wt%) was used. \*\*The crude liquid product containing toluene. \*\*\*GC area percent excluding toluene peak.

in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator<sup>2</sup> at carefully controlled temperatures between 260°C and 320°C.

Thus, a mixture of 90.0 g of metallic silicon (100-325 mesh) and 15.6 g of cuprous chloride (10% of copper by weight in the contact mixture) was placed in the reactor made of Pyrex glass tube, 25 mm in inner diameter and 400 mm in length, with a electrical heating wire coiled outside and equipped with a spiral band agitator.<sup>2b</sup> The mixture was dried at 250°C for 3 hours with stirring by dry nitrogen flush. Then the temperature was raised to and kept at 370°C for 2 hours for sintering between metallic silicon and catalyst to give a Si-Cu  $\eta$ -phase contact mixture. After removing tetrachlorosilane formed during the sintering process, the temperature was lowered to the desired reaction temperature, e.g. 280°C,  $\alpha,\alpha'$ -dichloro-*o*-xylene in toluene (47.65% w/w) was added using a syringe pump into the head of the reactor at the rate of 10 ml/hr. Nitrogen flow rate was controlled to 100 ml/min by Matheson 600 flowmeter to push the reactant and the products as well. The products were collected in the receiver at the bottom of the reactor. From the reaction of 50.41 g of the toluene solution containing 24.02 g of  $\alpha,\alpha'$ -dichloro-*o*-xylene, 14.20 g of I was isolated by vacuum distillation (yield, 51%).<sup>6</sup> Identified minor products were  $\alpha$ -trichlorosilyl-*o*-xylene (II, 2%), *o*-xylene (III, 3%), and 5, 6, 11, 12-tetrahydrodibenzo[*a,e*]cyclooctene (IV, 3%). The rest 41% of the reactant was converted due to decomposition to solid materials coagulating with silicon metal on the top of the reaction mass.



In order to check the temperatures effect for the direct

reaction, the reactions were carried out at various temperatures from 260°C to 320°C and the results are shown in Table 1. Although the highest yield of I was obtained at the reaction temperature of 280°C, the total amount of products and the percentage of I were not changed much as the temperature changed. The low yield of I in this reaction was due to the thermal instability of  $\alpha,\alpha'$ -dichloro-*o*-xylene.

Since co-catalyst, even in small amount, can influence greatly to the products distribution in direct reactions,<sup>2a</sup> we tested the effect of zinc, cadmium, or silver as a promoter by adding 0.5% of the total mass. Zinc, known as a good promoter for the direct synthesis of methylchlorosilanes<sup>7</sup> was accelerating the decomposition of the reactant so rapidly that the contact mixture was coagulated and could not be agitated. Cadmium, known as a good promoter for the direct reaction of  $\alpha$ -chloromethylsilanes,<sup>2b,c</sup> showed no significant effect in this work and neither the silver.

In conclusion, we report a novel convenient direct synthetic route for 2,2-dichloro-2-silaindan which is a strong candidate as a starting material for ring opening polymerization employing readily available starting materials and mild reaction conditions, and which can be used for a large scale production. This is the first example for the direct reaction of metallic silicon with benzylic chloride containing compound.

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6. The yield was calculated for the isolated mole percent, based on  $\alpha,\alpha'$ -dichloro-*o*-xylene reacted. For I; bp. 94-5°C/4 torr; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  2.64 (s, 4H, CH<sub>2</sub>), 7.18-7.30 (m, 4H, ArH).
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