

**NOVEL AND FACILE SYNTHESSES OF T-BUTYL SUBSTITUTED SILANES FROM T-BUTYL  
MAGNESIUM CHLORIDE AND CHLOROSILANES CATALYZED BY CUPROUS CYANIDE**

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**Summary:** t-Butyl substituted silanes, e.g. t-butyldimethylchlorosilane, were successfully obtained by cuprous chloride promoted coupling reaction of t-butyl Grignard reagent and chlorosilanes.

It has been thought for a long time that tertially alkyl Grignard reagents such as t-butyl magnesium chloride don't react with chlorosilanes such as dimethyldichlorosilane, methyltrichlorosilane and tetrachlorosilane under normal conditions.<sup>1</sup> Therefore, tertially alkyl lithium has been usually applied to make tertially alkyl substituted silanes from chlorosilanes.<sup>2,3</sup>

Among the tertially alkyl substituted silanes, t-butyldimethylchlorosilane is a widespread reagent for the protection of alcohols<sup>4</sup> and is also prepared by the reaction of dimethyldichlorosilane with t-butyl lithium, which is so hazardous that the price of the useful silylating reagent remains expensive.

Recently the substitution of chlorosilanes by Grignard reagent to afford tetraalkyl and tetraarylsilanes was reported.<sup>5</sup> According to the report, the reaction succeeded under mild conditions by the presence of cyanide or thiocyanate ions even when long chained alkyl Grignard reagents were applied.

It is here reported that the reaction of t-butyl Grignard reagent with chlorosilanes is also promoted by cuprous cyanide to give t-butyl substituted silanes at an ambient temperature. The results were summarized in Table 1.

t-Butyldimethylchlorosilane was obtained as follows; into a solution of t-butyl magnesium chloride in tetrahydrofuran (THF) prepared by using 46.3g (0.5mol) of t-butyl chloride, 12.2g (0.5mol) of magnesium and 200ml of THF, 0.45g (0.005 mol) of cuprous cyanide was added, followed by the dropwise addition of 63g (0.49 mol) of dimethyldichlorosilane, and the mixture was refluxed for 2 hrs.. The resulting mixture was filtered and the filtrate was distilled to give 55g (74% yield) of t-butyldimethylchlorosilane.

Using cuprous chloride, the formation of small amount of t-butyldimethylchlorosilane was observed. The active species which reacts with chlorosilanes is thought to be an alkyl copper complex. However, cyanide ion obviously accelerates and/or promotes the desired reaction. It is suggested that chlorosilanes react with cyanide ion to be pentacoordinate intermediates noted in literatures,<sup>5,6</sup> which enhance the reactivity toward nucleophiles and also possess sterically less hindered reactive sites on Si where t-butyl anion can approach.

**Table 1.** Reaction of t-butyl magnesium chloride with chlorosilanes

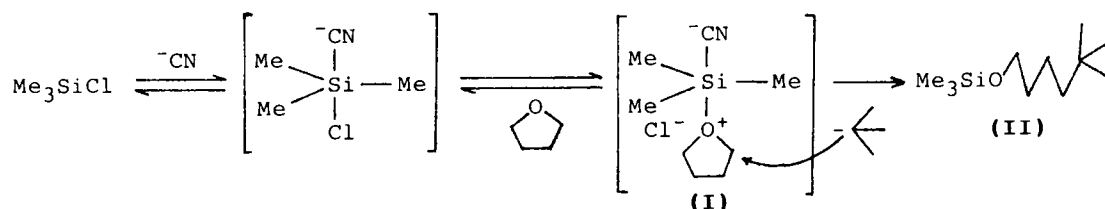
Run	Chlorosilane	Cat. <sup>a</sup>	Reaction condition	Product	Yield <sup>b</sup>
1	Me <sub>2</sub> SiCl <sub>2</sub>	CuCN	THF reflux, 2hrs.	t-BuMe <sub>2</sub> SiCl	74%
2	Me <sub>2</sub> SiCl <sub>2</sub>	CuCl	THF reflux, 3hrs.	t-BuMe <sub>2</sub> SiCl	13% <sup>c</sup>
3	Ph <sub>2</sub> SiCl <sub>2</sub>	CuCN	THF reflux, 5hrs.	t-BuPh <sub>2</sub> SiCl	80%
4	MeSiCl <sub>3</sub>	CuCN	THF rt., 2hrs.	t-BuMeSiCl <sub>2</sub>	53%
5	Me <sub>3</sub> SiCl	CuCN	THF reflux, 2hrs.	Me <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>4</sub> t-Bu	82%
6	Me <sub>3</sub> SiCl	CuCl	THF reflux, 4hrs.	Me <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>4</sub> t-Bu	30% <sup>c</sup>

a) 1 mol%

b) isolated yield unless otherwise noted

c) determined by GLC

When trimethylchlorosilane was used as a chlorosilane in this reaction, a coupling reaction in which the solvent participated was predominantly observed as shown in Table 1. The product, Me<sub>3</sub>SiO(CH<sub>2</sub>)<sub>4</sub>C(CH<sub>3</sub>)<sub>3</sub>, can be interpreted in the similar mechanism of the cleavage of ethers with iodotrimethylsilane.<sup>7</sup> Namely, a silyloxonium ion (I) is generated by the coordination of THF on the electrophilic pentacoordinate silicon atom, and t-butyl anion instead of iodo anion which works in the case of iodotrimethylsilane attacks the adjacent carbon of the oxonium ion, or an electron transfer occurs from t-butyl anion to the silyloxonium ion to be a radical ion pair followed by the coupling to produce Me<sub>3</sub>SiO(CH<sub>2</sub>)<sub>4</sub>C(CH<sub>3</sub>)<sub>3</sub> (II), as shown below.



**Acknowledgment.** The author greatly appreciates Professors Hideki Sakurai and Mitsuo Kira for helpful discussions.

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(Received in Japan 17 July 1989)