Convenient and Selective Preparation of Mono-alkoxyphenylsilanes from Phenylsilane and Alcohols

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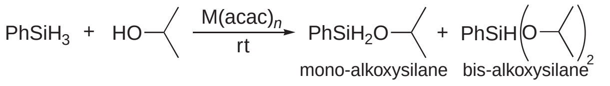
The selective dehydrogenative coupling of phenylsilane and alcohols, including primary, secondary, and tertiary alcohols, was smoothly catalyzed by bis(hexafluoroacetylacetonato)-copper(II) complex to afford the corresponding mono-alkoxysilanes in good-to-high yield after distillation.

Hydrosilanes are some of the most versatile reducing agents in organic synthesis.[1] Their combined use with various transition-metal complexes has provided many chemoselective or stereoselective synthetic reactions, for example, the hydrosilylation of ketones, imines,[2] or alkenes,[3] the silylformylation of alkenes,[4] etc. Hydrosilanes are also employed as a hydride source to generate metal hydrides.[5] In these synthetic reactions, the reactivities and selectivities can be tuned by the structures of the hydrosilanes, e.g., after the screening of various alkoxysilanes, the high yield and high enantioselectivity have been achieved for the enantioselective conjugated reaction catalyzed by Rh complex.[6] It was also noted that polymethylhydrosiloxane was employed in the place of tetramethyldisiloxane as the silane reducing agent to drastically improve the observed ee value for the hydrosilylation of imines catalyzed by Cu complex.[7] Therefore, preparative methods for the varieties of hydrosilane reagents are assumed to take more advantage for the tuning of these synthetic reactions and for the development of new methodologies using hydrosilanes. The dehydrogenative coupling of hydrosilanes and alcohols is one of the most preferable methods to prepare the alkoxysilanes, and various catalysts were reported for the dehydrogenative reaction including transition-metal complexes, inorganic salts, and Lewis acids.[8] Although the highly selective silylation of a primary alcohol over a secondary alcohol was recently reported with the catalytic use of Cu(I)–phosphine complex,[9] few reports have noted the mono-alkoxylation of trihydrosilanes to afford the mono-alkoxydihydrosilanes, and neither of them seemed to provide the efficient preparative methods for various alkoxysilanes.[10] It was also reported that $PdCl_2$ or $NiCl_2$ was used as a catalyst for the mono-alkoxylation of phenylsilane on the basis of its high reactivity but was unsuccessful.[11] In this communication, we report the convenient preparation of various alkoxydihydrosilanes from phenylsilane and the correspondig alcohols in the presence of a catalytic amount of the bis(hexafluoroacetylacetonato)copper(II) complex.

Various acetylacetonato metal complexes were first examined for the dehydrogenative coupling of phenylsilane and 2-propanol as a model reaction (Table 1). Without metal complexes, no reaction occurred. The Mg(II), Al(III), Ti(IV), V(IV), Cr(III), and Mn(II) acetylacetonato complexes had little activity for the reaction, which resulted in the slight conversion of phenylsilane. Although Mn(III), Fe(II), Co(II), Co(III), Ru(III), and Pt(II) were found to catalyze the dehydrogenative reaction, the major product was diisopropyloxyphenylsilane, generated by over-condensation of isopropyloxyphenylsilane with 2-propanol. Ni(II), Pd(II), and Rh(III) were active enough to achieve the complete consumption of phenylsilane, but the desired mono-alkoxysilane was scarcely remained. When bis(acetylacetonato)copper was employed, in contrast, the dehydrogenative coupling smoothly proceeded in good selectivity to afford isopropyloxyphenylsilane in 67% yield.

Table 1. Various acetylacetonato complexes[a]



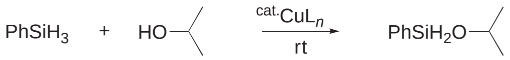
Entry	Metal	Time/h	Conv./%[b]	Mono:Bis	Yield/%[b]
1	None	2.5	1	—	1
2	Mn(III)	3.0	21	36:64	7
3	Fe(II)	7.0	32	12:88	4
4	Co(II)	0.67	53	17:83	9
5	Co(III)	6.0	67	14:86	9
6	Ru(III)	2.0	67	48:52	28
7	Pt(II)	4.0	49	50:50	18
8	Ni(II)	6.0	100	10:90	6
9	Rh(III)	2.5	100	95%[c]	0
10	Pd(II)	1.0	100	55%[c]	0
11	Cu(II)	1.0	75	89:11	67

[a]Phenylsilane, 1 mmol; 2-propanol, 10 mmol; metal, 0.1 mmol. [b]Determined by GC analysis and based on phenylsilane. [c]The yield of diisopropyloxyphenylsilane.

In the presence of 10 mol % of the various copper[12] complexes, various ligands were then screened (Table 2). Copper chloride, bromide, iodide, and acetate catalyzed the dehydrogenative reaction to afford the mono-alkoxysilane as the major product while the yields were moderate or low. Various 1,3-diketonato-type complexes were then examined. In each case, the selectivity and yield of the mono-alkoxyphenylsilane were not improved compared to the bis(acetylacetonato)copper. Reducing the loading amounts of the catalyst and the alcohol enabled one to control the reactivity in the reaction catalyzed by bis(hexafluoroacetylacetonato)copper(II) to afford the monoalkoxyphenylsilane with good selectivity. The optimization of the reaction conditions resulted in an improved product yield up to 86%.

The dehydrogenative coupling of phenylsilane and 2-propanol was successfully applied to the 10 mmol scale preparation with bis(hexafluoroacetylacetonato)copper(II) and the obtained crude material could be purified by distillation to give the desired product in 77% isolated yield.[13] The other secondary alcohols and primary alcohols could also be transformed to the corresponding mono-alkoxysilanes in good yields after distillation (Table 3). Although the bulky alcohol like *t*-butyl alcohol was less reactive, the increased use of the copper catalyst and alcohol afforded full conversion of the phenylsilane to provide the

Table 2. Various copper complexes[a]



Entry	CuL_n	Conv./%[b]	Mono:Bis[b]	Yield/%[b]
1	CuCl	92	87:13	73
2	$CuCl_2$	88	74:26	49
3	CuBr	93	68:32	59
4	$CuBr–Me_2S$	50	85:15	40
5	CuI	9	97: 3	8
6	$Cu(OAc)_2$	64	86:14	47
7	$Cu(paa)_2$	53	93: 7	39
8	$Cu(bza)_2$	85	80:20	65
9	$Cu(dpm)_2$	100	27%[c]	0
10	$Cu(tfh)_2$	85	3:97	2
11	$Cu(dmh)_2$	98	65:35	44
12	$Cu(tfa)_2$	60	77:23	46
13	$Cu(hfa)_2$	100	33%[c]	0
14[d]	$Cu(hfa)_2$ (1.0 mol %)	81	88:12	67
15[e]	$Cu(hfa)_2$ (1.5 mol %)	98	91: 9	86

[a]Phenylsilane, 1 mmol; 2-propanol, 10 mmol unless otherwise noted. [b]Determined by GC analysis. [c]The yield of diisopropyloxyphenylsilane. [d]2-Propanol, 1 equiv. [e]2-Propanol, 1.5 equiv.

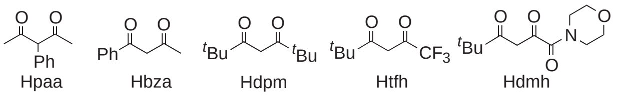
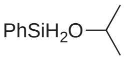
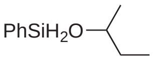
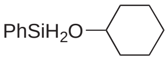
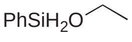
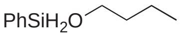
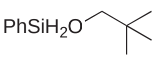
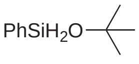


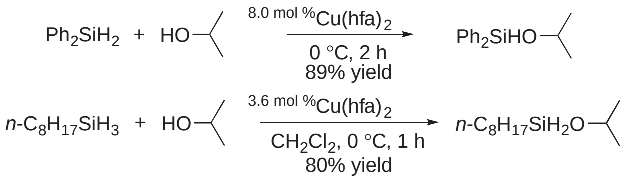
Table 3. Preparation of mono-alkoxyphenylsilanes[a]

$$PhSiH_3 + ROH \xrightarrow{cat.Cu(hfa)_2} PhSiH_2OR$$

Entry	Alkoxyphenylsilane	Conv./%	Yield/%	(Isolated)
1		95	83	(77)
2[b]		93	83	(66)
3[c]		88	75	(64)
4		97	75	(62)[d]
5[c]		86	71	(65)
6[e]		91	74	(68)
7[f]		97	95	(76)

[a]The reaction was carried out using 1.5 equiv. alcohol, 1.5 mol % of catalyst, and CH_2Cl_2 at 0 °C unless otherwise noted. [b]Catalyst, 2.3 mol %. [c]Catalyst, 2.0 mol %. [d]5.5:1 mixture of $PhSiH_2(OEt)$ and $PhSiH(OEt)_2$. [e]Catalyst, 3.0 mol %. [f]Catalyst, 5.0 mol %; t-butanol, 3.0 equiv.

mono-alkoxysilane with a high selectivity and yield. Octylsilane was also applicable for the dehydrogenative condensation, and the pure isopropyloxyoctylsilane was obtained in 80% yield in the same manner. While the coupling of diphenylsilane and 2-propanol needed both a greater excess of catalyst loading and neat conditions, the highly selective generation of the mono-alkoxysilane with 89% yield was observed (Scheme 1).



Scheme 1.

It is noted that trihydrosilanes were selectively transformed into dihydroalkoxysilanes by the dehydrogenative coupling with primary, secondary, and tertiary alcohols in the presence of a catalytic amount of bis(hexafluoroacetylacetonato)copper(II).

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13 Typical procedure: To the stirred solution of bis(hexafluoroacetylacetonato)copper(II) (143 mg, 0.3 mmol) in 2-propanol (2.30 mL, 30 mmol) and CH_2Cl_2 (7 mL) was added $PhSiH_3$ (2.47 mL, 20 mmol) in one portion at 0 °C under N_2. After stirring for 0.75 h at 0 °C, hexane (15 mL) was added and the existing solid was filtered off. The residue was concentrated under reduced pressure, then fractionally distilled using bulb-to-bulb distillation apparatus to give $PhSiH_2O^iPr$ (2.56 g, 77%) as a colorless oil.

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