



Convenient synthesis of alkoxyhalosilanes from hydrosilanes

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Abstract

Selective dehydrogenative coupling of di- and trihydrosilanes with alcohols catalyzed by PdCl₂ or NiCl₂ afforded alkoxyhydro- and dialkoxyhydrosilanes in good yield. Further treatment of the resulting alkoxyhydrosilanes with carbon tetrachloride or allyl bromide in the presence of the same catalyst led to the formation of alkoxychloro- and alkoxybromosilanes, respectively. Similar reactions of dialkoxyhydrosilanes with carbon tetrachloride afforded dialkoxychlorosilanes in good yield, although contamination of small amounts of trialkoxysilanes and alkoxydichlorosilanes was detected in the products. Selective substitution of the alkoxyhalosilanes with nucleophiles is also reported.

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1. Introduction

Organohalo- and alkoxyhalosilanes are important reagents as the building units for a variety of organosilicon compounds [1]. Reactions with carbon nucleophiles with halo- and alkoxyhalosilanes provide direct routes to form C–Si bonds. However, the selectivity of substitution reactions at dihalo- and dialkoxyhalosilanes is not always high, unless steric requirement prevents the second molecule of the nucleophile from approaching the silicon center [1]. Recently, we reported the synthesis of chlorofluorosilanes from selective and successive halogenation of dihydrosilanes [2]. As expected, their substitution reactions proceed selectively and only the Si–Cl bond is substituted upon interaction with 1 equiv. of a nucleophile, leaving the Si–F bond intact [3].

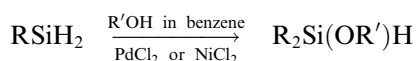
In this paper, we report convenient synthesis of alkoxyhalosilanes by selective transformation of hydrosilanes. These compounds may be anticipated as useful organosilicon reagents and their bifunctionalities seem to allow selective transformation around the silicon atom, similar to chlorofluorosilanes. Although mono-substitution of dihalosilanes with alcohols is generally used for the synthesis of alkoxyhalosilanes, this involves the production of a quantitative amount of hydrogen halide that may contaminate the products. Tertiary amines are often used to remove the hydrogen halides as the ammonium salts. However, the formation of the ammonium salts that tend to remain in the organic mixtures often makes distillation of the products difficult, due to the formation of a large amount of residue and by sublimation of the salts. The present method involves dehydrogenative coupling of hydrosilanes with alcohols, followed by H-halogen exchange of the resulting alkoxyhydrosilanes with alkyl halides, and thus seems to be convenient, clean, and useful for the preparation of alkoxyhalosilanes.

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2. Results and discussion

2.1. Selective alkoxylation of di- and trihydrosilanes

Table 1 summarizes the results of selective formation of alkoxyhydrosilanes from dihydrosilanes. Thus, the PdCl₂-catalyzed reactions of dihexylsilane with 1 equiv. of methanol or ethanol in benzene or toluene gave the corresponding alkoxyhydrosilanes in good isolated yield. In these reactions, 1–2% of dialkoxysilanes, that were readily removed by fractional distillation, were found to be formed by GC–MS analysis. Diphenylsilane also reacted with alcohols in the presence of the PdCl₂ catalyst, but less selectively, giving 6–7% of dialkoxysilanes together with the expected mono-substitution products. Using NiCl₂ as the catalyst, however, led to higher selectivity of the reactions to raise the yields, although the NiCl₂-catalyzed reactions proceeded more slowly than the PdCl₂-catalyzed ones and required heating the reaction mixtures for longer period with a larger amount of the catalyst.



R = Hex, Ph

R' = Me, Et

In the present reactions, the formation of fine black precipitates was observed, immediately after the contact of the reactants with the catalysts. This seems to indicate that the actual active species in these reactions were Pd(0) and Ni(0) metals, respectively, arising from the reduction of the chlorides with dihydrosilanes, similar

to halogenation of hydrosilanes with alkyl halides in the presence of the same catalysts, reported previously [4]. Although we have not yet obtained clear evidences concerning the reaction mechanism, the homolytic Si–H bond cleavage would occur on the metal surface, generating silyl radicals as the key intermediates. Metathesis type reactions on the metal surface may also be involved. The selective formation of mono-substitution products in the present reactions primarily presumably owes to the steric protection of the Si–H unit by the initially introduced alkoxy group. Another alternative comprises the nucleophilic attack of alcohols to hydrosilanes activated on the metal surface, as proposed for similar Pd–C catalyzed dehydrogenative coupling of hydrosilanes with alcohols by Sommer and Lyons [5]. In this case, however, it was reported that alkoxyhydrosilanes reacted more rapidly than the corresponding dihydrosilanes, in contrast to our observations, making this alternative improbable for the present reactions.

Although similar base-catalyzed selective transformation of dihydrosilanes to alkoxyhydrosilanes has been well studied [6], a large amount of the base is usually required. It is also known that some transition-metal-complexes, such as RhCl(PPh₃)₃, catalyze the transformation [7]. However, the present method using less expensive heterogeneous catalysts seems to be potentially useful.

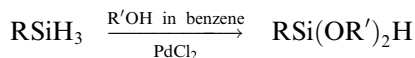
Treatment of dihydrosilanes with 2 equiv. of methanol or ethanol under the same conditions as the mono-substitution reactions gave dialkoxysilanes in good isolated yield. Attempted mono-substitution of trihydrosilanes failed and their PdCl₂- or NiCl₂-catalyzed

Table 1
Dehydrogenative coupling of hydrosilanes with alcohols

Silane (amount, mmol)	Alcohol (eq)	Catalyst (%)	Temperature (°C)	Time (h)	Product	Yield (%)	
						Isolated	GC ^a
Hex ₂ SiH ₂ (29.2) (17.1) (20.5) (15.0) (3.0)	EtOH (1.0)	PdCl ₂ (0.1)	25	24	Hex ₂ Si(OEt)H	88	99 (1)
	EtOH (1.0)	NiCl ₂ (2.5)	60	72		79	97 (2)
	EtOH (3.3)	PdCl ₂ (0.1)	25	1	Hex ₂ Si(OEt) ₂	87	
	MeOH (1.0)	PdCl ₂ (0.2)	25	24	Hex ₂ Si(OMe)H	84	96 (2)
	MeOH (5.1)	PdCl ₂ (0.2)	25	1	Hex ₂ Si(OMe) ₂	74	
Ph ₂ SiH ₂ (12.4) (25.7) (13.5) (17.2) (30.9)	EtOH (1.0)	PdCl ₂ (0.2)	25	24	Ph ₂ Si(OEt)H	65	92 (6)
	EtOH (1.0)	NiCl ₂ (3.6)	60	72		72	96 (3)
	MeOH (1.0)	PdCl ₂ (0.1)	25	24	Ph ₂ Si(OMe)H	69	91 (7)
	MeOH (1.0)	NiCl ₂ (3.6)	60	72		74	99 (1)
	MeOH (3.0)	PdCl ₂ (0.1)	25	72	Ph ₂ Si(OMe) ₂	71	
HexSiH ₃ (91.1) (23.2) (50.8)	EtOH (2.0)	PdCl ₂ (0.1)	25	3	HexSi(OEt) ₂ H	80	
	EtOH (3.1)	PdCl ₂ (0.2)	25	3	HexSi(OEt) ₃	83	
	MeOH (2.0)	PdCl ₂ (0.1)	25	15	HexSi(OMe) ₂ H	70	
PhSiH ₃ (81.6) (24.7) (54.3)	EtOH (2.0)	PdCl ₂ (0.1)	25	19	PhSi(OEt) ₂ H	79	
	EtOH (3.2)	PdCl ₂ (0.2)	25	1	PhSi(OEt) ₃	90	
	MeOH (2.0)	PdCl ₂ (0.1)	25	9	PhSi(OMe) ₂ H	74	

^a Determined by GC. Numbers in parentheses are yields of disubstituted products.

reactions with 1 equiv. of ethanol gave mixtures of the corresponding mono- and dialkoxysilane, and the starting compound. However, selective di-substitution of trihydrosilanes was successfully performed with 2 equiv. of ethanol or methanol in the presence of PdCl₂, giving dialkoxyhydrosilanes exclusively as shown in Table 1. Treatment of trihydrosilanes with 3 equiv. of ethanol gave triethoxysilanes in high yield.

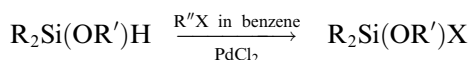


R = Hex, Ph

R' = Me, Et

2.2. Preparation of alkoxyhalosilanes

Treatment of alkoxyhydrosilanes with CCl₄ [8] or allyl bromide [4] afforded the chlorinated and brominated products, respectively (Table 2). Alkoxychlorosilanes were readily separated from the reaction mixtures by distillation in pure form, while alkoxybromosilanes could not be isolated, due to their strong tendency to undergo hydrolysis even with atmospheric moisture. The formation of alkoxybromosilanes, therefore, was confirmed by transformation of them to more stable alkoxytrialkylsilanes by the reactions with 1 equiv. of nucleophiles (see Section 2.3).



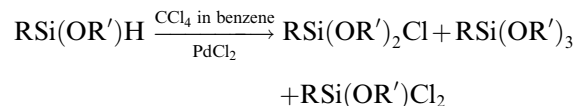
R = Hex, Ph

X = Cl, Br

R' = Me, Et

Similar reactions of dimethoxyhydrosilanes with CCl₄ under the same conditions, followed by fractional distillation, afforded dimethoxychlorosilanes in good yield. However, contamination of 2–3% of trimethoxy- and dichloromethoxysilanes that could not be separated from chlorodimethoxysilanes by distillation was detected by the GC–MS analysis of the distilled prod-

ucts. Halogenation of diethoxyhydrosilanes proceeded less selectively, leading to the formation of triethoxy- and dichloroethoxysilanes in higher yields (ca. 10% yields each), although expected products, chlorodiethoxysilanes, were found to be formed in approximately 80% yield by GC–MS analysis of the reaction mixtures.

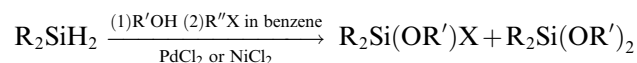


R = Hex, Ph

R' = Me, Et

For the formation of alkoxyhalosilanes, it was not necessary to isolate the alkoxyhydrosilanes.

Thus, as presented in Table 3, when dihydrosilanes were treated with 1 equiv. of alcohols and then with CCl₄ or allyl bromide and an additional amount of the catalyst was added to the resulting mixtures containing alkoxyhydrosilanes, alkoxyhalosilanes were obtained in good yield, although contamination of 1–7% of dialkoxysilanes could not be avoided (Table 3).



R = Hex, Ph

X = Cl, Br

R' = Me, Et

2.3. Reactions of alkoxyhalosilanes

As expected, reactions of alkoxyhalosilanes with 1 equiv. of nucleophiles proceeded selectively to give mono-substitution products in good yield (Table 4). Treatment of Hex₂Si(OMe)Cl with 1 equiv. of *n*-BuLi at –50 °C afforded an 89% yield of a mixture of Hex₂Si(OMe)Bu/Hex₂SiClBu = 98/2. The selectivity was improved by lowering the reaction temperature and no formation of the corresponding chloride was detected in the reaction at –78 °C. Similar reactions of less

Table 2
Preparation of alkoxyhalosilanes

Silane (amount, mmol)	Halide (eq)	PdCl ₂ (%)	Temperature (°C)	Time (h)	Product	Yield (%)
Hex ₂ Si(OEt)H (12.7)	CCl ₄ (1.0)	0.3	25	24	Hex ₂ Si(OEt)Cl	79 ^a
(4.6)	AllylBr (1.0)	0.8	60	6	Hex ₂ Si(OEt)Br	88 ^b
Hex ₂ Si(OMe)H (10.8)	CCl ₄ (1.0)	0.3	25	11	Hex ₂ Si(OMe)Cl	81 ^a
Ph ₂ Si(OEt)H (20.6)	CCl ₄ (1.0)	0.3	25	15	Ph ₂ Si(OEt)Cl	79 ^a
(6.1)	AllylBr (1.0)	0.9	60	14	Ph ₂ Si(OEt)Br	89 ^b
Ph ₂ Si(OMe)H (9.0)	CCl ₄ (1.0)	0.3	25	24	Ph ₂ Si(OMe)Cl	73 ^a
Hex(OMe) ₂ SiH (11.3)	CCl ₄ (1.0)	0.4	25	5	HexSi(OMe) ₂ Cl	82 (95 ^c)
Ph(OMe) ₂ SiH (17.2)	CCl ₄ (1.0)	0.4	25	9	PhSi(OMe) ₂ Cl	76 (96 ^c)

^a Isolated yield.

^b GC yield.

^c Purity (%) of the distilled product determined by GC.

Table 3
One-pot synthesis of alkoxyhalosilanes from dihydrosilanes

Silane (amount, mmol)	Catalyst	Alcohol (catalyst, %)	Halide (catalyst, % ^a)	Product	Yield	
					%	Ratio ^c
Hex ₂ SiH ₂ (25.7) (12.4) (13.9)	PdCl ₂	EtOH (0.2)	CCl ₄ (0.4)	Hex ₂ Si(OEt)Cl	79	95/5
	PdCl ₂	EtOH (0.1)	AllylBr (0.4)	Hex ₂ Si(OEt)Br	91 ^b	93/7
	PdCl ₂	MeOH (0.2)	CCl ₄ (0.7)	Hex ₂ Si(OMe)Cl	76	99/1
Ph ₂ SiH ₂ (29.1) (10.8)	NiCl ₂	EtOH (3.5)	CCl ₄ (6.0)	Ph ₂ Si(OEt)Cl	76	94/6
	NiCl ₂	MeOH (3.5)	CCl ₄ (7.0)	Ph ₂ Si(OMe)Cl	62	93/7

^a Total amount of the catalyst. An additional amount of the catalyst must be added to promote the halogenation.

^b GC yield.

^c Ratio of R₂Si(OR')X/R₂Si(OR')₂ of the distilled product determined by GC.

Table 4
Reactions of alkoxyhalosilanes with nucleophiles

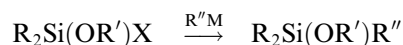
Reactant	Nucleophile	Temperature (°C)	Product	Yield (%) ^a
Hex ₂ Si(OMe)Cl	<i>n</i> -BuLi	-50	Hex ₂ Si(OMe) <i>n</i> -Bu	89 ^b
		-78	Hex ₂ Si(OMe) <i>n</i> -Bu	86
Hex ₂ Si(OEt)Cl	<i>n</i> -BuLi	-78	Hex ₂ Si(OEt) <i>n</i> -Bu	83
		-78	Hex ₂ Si(OEt)C≡CPh	78
		-78	Hex ₂ Si(OEt)CH=CH ₂	80
Ph ₂ Si(OEt)Cl	<i>n</i> -BuLi	-78	Ph ₂ Si(OEt) <i>n</i> -Bu	74
		-78	Ph ₂ Si(OEt)C≡CPh	49
		-78	Ph ₂ Si(OEt)CH=CH ₂	69
Hex ₂ Si(OEt)Br	<i>n</i> -BuLi	-70	Hex ₂ Si(OEt) <i>n</i> -Bu	79 ^c
		-78	Hex ₂ Si(OEt)C≡CPh	76 ^c
		-78	Hex ₂ Si(OEt)CH=CH ₂	71 ^c
Ph ₂ Si(OEt)Br	<i>n</i> -BuLi	-70	Ph ₂ Si(OEt) <i>n</i> -Bu	74 ^c

^a Isolated yield.

^b Hex₂Si(OMe)*n*-Bu/Hex₂Si(Cl)*n*-Bu = 98/2.

^c Yield based on the starting ethoxyhydrosilane.

hindered vinylmagnesium chloride in THF again gave mono-substitution products, selectively. With even less sterically hindered phenylethynyllithium, Hex₂Si(OEt)(C≡CPh) was obtained in 78% isolated yield. In this reaction, again no disubstitution took place, in marked contrast to that of Hex₂SiCl₂ with PhC≡CLi under the same conditions, which gave a mixture of PhC≡CSiHex₂Cl, (PhC≡C)₂SiHex₂, and the starting Hex₂SiCl₂ in a ratio of 17:42:41. Dialkoxysilane Hex₂Si(OEt)₂ did not react with PhC≡CLi at all at low temperature. Reactions of Ph₂Si(OEt)Cl and bromo-(ethoxy)silanes, Hex₂Si(OEt)Br and Ph₂Si(OEt)Br with 1 equiv. of nucleophiles also proceeded selectively to give mono-substituted alkoxyhalosilanes.



R = Hex, Ph

X = Cl, Br

R' = Me, Et

In conclusion, we demonstrated that selective alkoxylation of dihydro- and trihydrosilanes, followed by halogenation, could be a convenient method for the preparation of alkoxyhalo- and dialkoxyhalosilanes that seemed to be useful reagents for the synthesis of a variety of organosilicon compounds.

3. Experimental

3.1. General procedures

All reactions were carried out under an atmosphere of dry nitrogen. Benzene, CCl₄, and allyl bromide were dried over P₂O₅ and distilled just before use. Diethyl ether and toluene were dried over sodium and distilled just before use. Alcohols were dried over the respective magnesium alkoxide and distilled just before use. NMR spectra were measured in CDCl₃ at ambient temperature.

3.2. Alkoxylation of di- and trihydrosilanes

A mixture of Hex_2SiH_2 (5.85 g, 29.2 mmol), EtOH (13.38 g, 29.1 mmol), and PdCl_2 (0.007 g, 0.039 mmol) in 75 mL of benzene was stirred at room temperature for 24 h. After the resulting black precipitates were filtered, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give $\text{Hex}_2\text{Si}(\text{OEt})\text{H}$ (6.22 g, 25.6 mmol; 88% yield): b.p. 75 °C, 1 mmHg; IR 2097 cm^{-1} (Si–H); ^1H NMR δ 4.33 (quintet, $J = 2.4$ Hz, 1H, SiH), 3.59 (q, $J = 7.0$ Hz, 2H, CH_2O), 1.30–1.07 (m, 19H, CH_2C_2 in Hex and CH_3 in OEt), 0.76 (t, $J = 7.0$ Hz, 6H, CH_3 in Hex), 0.55 (br t, $J = 7.2$ Hz, 4H, $\text{CH}_2\text{–Si}$); ^{13}C NMR δ 60.13 (CH_2O), 32.81, 31.56, 23.09, 22.57 (Hex), 18.26 (CH_3 in EtO), 14.09, 13.82 (Hex); GC–MS m/z 244 (M^+). Anal. Calc. for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$: C, 68.77; H, 13.19. Found: C, 68.56; H, 13.19%.

The other partial alkoxylation of di- and trihydrosilanes was carried out as above. Data for $\text{Hex}_2\text{Si}(\text{OMe})\text{H}$: b.p. 65 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); IR 2098 cm^{-1} ; ^1H NMR δ 4.42 (quintet, $J = 2.3$ Hz, 1H), 3.48 (s, 3H), 1.45–1.15 (m, 16H), 0.88 (t, $J = 7.0$ Hz, 6H), 0.67 (br t, $J = 7.0$, 4H); ^{13}C NMR δ 52.20, 32.81, 31.54, 23.08, 22.55, 14.05, 13.43; GC–MS m/z 230 (M^+). Anal. Calc. for $\text{C}_{13}\text{H}_{30}\text{OSi}$: C, 67.75; H, 13.12. Found: C, 67.86; H, 13.11%. Data for $\text{Ph}_2\text{Si}(\text{OEt})\text{H}$: b.p. 83–85 °C, 1 mmHg; IR 2122 cm^{-1} ; ^1H NMR δ 7.73 (dd, $J = 7.7$, 1.7 Hz, 4H, *o*-Ph), 7.50–7.23 (m, 6H, *m*- and *p*-Ph), 5.42 (s, 1H, SiH), 3.85 (q, $J = 6.9$ Hz, 2H, CH_2), 1.25 (t, $J = 6.9$ Hz, 3H, CH_3); ^{13}C NMR δ 134.65 (CH in Ph), 134.32 (*ipso*-C in Ph), 130.30, 128.01 (CH in Ph), 60.58 (CH_2), 18.13 (CH_3); GC–MS m/z 228 (M^+). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{OSi}$: C, 73.63; H, 7.06. Found: C, 73.42; H, 7.07%. Data for $\text{Ph}_2\text{Si}(\text{OMe})\text{H}$: b.p. 63–65 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); IR 2118 cm^{-1} ; ^1H NMR δ 7.65 (dd, $J = 7.7$, 1.7 Hz, 4H), 7.48–7.37 (m, 6H), 5.41 (s, 1H), 3.63 (s, 3H); ^{13}C NMR δ 134.63, 133.60, 130.40, 128.05, 52.45; GC–MS m/z 214 (M^+). Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{OSi}$: C, 72.85; H, 6.58. Found: C, 72.87; H, 6.54%. Data for $\text{HexSi}(\text{OEt})_2\text{H}$: b.p. 45 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); IR 2151 cm^{-1} ; ^1H NMR δ 4.50 (br t, $J = 1.7$ Hz, 1H), 3.80 (q, $J = 6.9$ Hz, 4H), 1.28–1.17 (m, 14H), 0.87 (br t, $J = 6.9$ Hz, 3H), 0.65 (br t, $J = 7.2$ Hz, 2H); ^{13}C NMR δ 59.32, 32.54, 31.52, 22.54, 22.07, 18.26, 14.09, 13.34; GC–MS m/z 204 (M^+). Anal. Calc. for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{Si}$: C, 58.77; H, 11.84. Found: C, 58.49; H, 11.89%. Data for $\text{HexSi}(\text{OMe})_2\text{H}$: b.p. 80 °C, 20 mmHg (oven temperature on Kugel-rohr distillation); ^1H NMR (δ in CDCl_3) 4.44 (br t, $J = 1.4$ Hz, 1H), 3.54 (s, 6H), 1.39–1.18 (m, 8H), 0.86 (t, $J = 6.8$ Hz, 3H), 0.67–0.63 (m, 2H); ^{13}C NMR (δ in CDCl_3) 51.25, 32.54, 31.49, 22.51, 21.88, 14.07, 12.76; GC–MS m/z 176 (M^+). Anal. Calc. for $\text{C}_8\text{H}_{20}\text{O}_2\text{Si}$: C,

54.49; H, 11.43. Found: C, 54.25; H, 11.41%. Data for $\text{PhSi}(\text{OEt})_2\text{H}$: b.p. 40 °C, 1 mmHg; IR 2162 cm^{-1} ; ^1H NMR δ 7.64 (dd, $J = 7.7$, 1.2 Hz, 2H), 7.48–7.34 (m, 3H), 4.93 (s, 1H), 3.89 (q, $J = 7.0$ Hz, 4H), 1.26 (br t, $J = 7.0$ Hz, 6H); ^{13}C NMR δ 134.03, 133.10, 130.57, 127.94, 59.44, 18.23; GC–MS m/z 196 (M^+). Anal. Calc. for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Si}$: C, 61.18; H, 8.22. Found: C, 61.06; H, 8.24%. Data for $\text{PhSi}(\text{OMe})_2\text{H}$: b.p. 40 °C, 1 mmHg; ^1H NMR δ 7.61 (dd, $J = 7.7$, 1.2 Hz, 2H), 7.47–7.36 (m, 3H), 4.86 (s, 1H), 3.61 (s, 6H); ^{13}C NMR δ 133.92, 132.12, 130.75, 128.00, 51.18; GC–MS m/z 168 (M^+). Anal. Calc. for $\text{C}_8\text{H}_{12}\text{O}_2\text{Si}$: C, 57.10; H, 7.19. Found: C, 57.08; H, 7.23%.

Peralkoxylation of di- and trihydrosilanes was performed in a similar fashion to monoalkoxylation, using a small excess of methanol or ethanol. Data for $\text{Hex}_2\text{Si}(\text{OEt})_2$: b.p. 120 °C, 1 mmHg; ^1H NMR δ 3.72 (q, $J = 6.9$ Hz, 4H), 1.55–1.17 (m, 22H), 0.87 (br t, $J = 6.6$ Hz, 6H), 0.57 (br t, $J = 7.2$ Hz, 4H); ^{13}C NMR δ 58.08, 33.10, 31.61, 22.88, 22.59, 18.26, 14.59, 14.09; GC–MS m/z 288 (M^+). Anal. Calc. for $\text{C}_{16}\text{H}_{36}\text{O}_2\text{Si}$: C, 66.60; H, 12.58. Found: C, 66.55; H, 12.55%. Data for $\text{Hex}_2\text{Si}(\text{OMe})_2$: b.p. 80 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ^1H NMR δ 3.51 (s, 6H), 1.42–1.15 (m, 16H), 0.87 (t, $J = 7.0$ Hz, 6H), 0.56 (br t, $J = 7.3$ Hz, 4H); ^{13}C NMR δ 50.23, 33.05, 31.50, 22.64, 22.55, 14.07, 11.92; GC–MS m/z 260 (M^+). Anal. Calc. for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$: C, 64.55; H, 12.38%. Found: C, 63.96; H, 12.36. Data for $\text{Ph}_2\text{Si}(\text{OMe})_2$: b.p. 110 °C, 1 mmHg; ^1H NMR δ 7.67 (dd, $J = 7.7$, 1.7 Hz, 4H), 7.41–7.38 (m, 6H), 3.64 (s, 6H); ^{13}C NMR δ 134.83, 132.27, 130.35, 127.91, 50.93; GC–MS m/z 244 (M^+). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Si}$: C, 68.81; H, 6.60. Found: C, 68.71; H, 6.66%. Data for $\text{HexSi}(\text{OEt})_3$: b.p. 50 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ^1H NMR δ 3.80 (q, $J = 7.0$ Hz, 6H), 1.60–1.28 (m, 17H), 0.86 (br t, $J = 7.0$ Hz, 3H), 0.62 (br t, $J = 7.2$ Hz, 2H); ^{13}C NMR δ 58.28, 32.83, 31.48, 22.72, 22.55, 18.28, 14.07, 10.42; GC–MS m/z 248 (M^+). Anal. Calc. for $\text{C}_{12}\text{H}_{28}\text{O}_3\text{Si}$: C, 57.92; H, 11.34. Found: C, 57.63; H, 11.60%. Data for $\text{PhSi}(\text{OEt})_3$: b.p. 70 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ^1H NMR δ 7.66 (dd, $J = 7.7$, 1.7 Hz, 2H), 7.42–7.28 (m, 3H), 3.86 (q, $J = 6.9$ Hz, 6H), 1.24 (t, $J = 6.9$ Hz, 9H); ^{13}C NMR δ 134.79, 130.96, 130.30, 127.82, 58.71, 18.21; GC–MS m/z 240 (M^+). Anal. Calc. for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Si}$: C, 59.96; H, 8.39. Found: C, 59.88; H, 8.37%.

3.3. Chlorination of alkoxyhydrosilanes

A mixture of $\text{Hex}_2\text{Si}(\text{OEt})\text{H}$ (3.08 g, 12.7 mmol), CCl_4 (1.97 g, 12.8 mmol), and PdCl_2 (0.0067 g, 0.038 mmol) in 25 mL of toluene was stirred at room temperature for 24 h. After the resulting black precipitates were filtered, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give

Hex₂Si(OEt)Cl (2.79 g, 10.0 mmol; 79% yield): b.p. 90–95 °C, 1 mmHg; ¹H NMR δ 3.70 (q, *J* = 7.3 Hz, 2H), 1.31–1.09 (m, 19H), 0.78–0.71 (m, 10H); ¹³C NMR δ 59.19, 32.56, 31.41, 22.79, 22.50, 18.46, 16.80, 14.05; GC–MS *m/z* 278 (M⁺). Anal. Calc. for C₁₄H₃₁ClOSi: C, 60.28; H, 11.20. Found: C, 60.22; H, 11.15%.

The other chlorination of alkoxyhydrosilanes was carried out as above. Data for Hex₂Si(OMe)Cl: b.p. 80 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR δ 3.53 (s, 3H), 1.42–1.20 (m, 16H), 0.93–0.78 (m, 10H); ¹³C NMR δ 50.87, 32.56, 31.52, 22.51, 22.44, 16.37, 14.05; GC–MS *m/z* 233 (M⁺–OMe). Anal. Calc. for C₁₃H₂₉ClOSi: C, 58.94; H, 11.04. Found: C, 58.96; H, 11.08%. Data for Ph₂Si(OEt)Cl: b.p. 90 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR δ 7.60 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.51–7.23 (m, 6H), 3.92 (q, *J* = 6.9 Hz, 2H), 1.29 (t, *J* = 6.9 Hz, 3H); ¹³C NMR δ 134.39, 131.73, 130.98, 128.07, 60.02, 17.85; GC–MS *m/z* 262 (M⁺). Anal. Calc. for C₁₄H₁₅ClOSi: C, 63.98; H, 5.75. Found: C, 63.95; H, 5.74%. Data for Ph₂Si(OMe)Cl: b.p. 80–85 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR δ 7.69 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.51–7.33 (m, 6H), 3.67 (s, 3H); ¹³C NMR δ 134.41, 132.09, 131.12, 128.14, 51.50; GC–MS *m/z* 248 (M⁺). Anal. Calc. for C₁₃H₁₃ClOSi: C, 62.76; H, 5.27. Found: C, 62.59; H, 5.37%. Data for HexSi(OMe)₂Cl (95% pure, containing 2% of HexSi(OMe)₃ and 3% of HexSi(OMe)Cl₂): b.p. 40 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR (δ in CDCl₃) 3.58 (s, 6H), 1.44–1.22 (m, 8H), 0.87–0.82 (m, 5H); ¹³C NMR (δ in CDCl₃) 51.17, 32.24, 31.37, 22.47, 22.25, 14.37, 14.05; GC–MS *m/z* 210 (M⁺). Anal. Calc. for C₈H₁₉ClO₂Si: C, 45.59; H, 9.09. Found: C, 45.74; H, 9.12%. Data for PhSi(OMe)₂Cl (96% pure, containing 2% of PhSi(OMe)₃ and 2% of PhSi(OMe)Cl₂): b.p. 45 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR (δ in CDCl₃) 7.69–7.66 (m, 2H), 7.50–7.38 (m, 3H), 3.67 (s, 6H); ¹³C NMR (δ in CDCl₃) 134.20, 131.45, 129.72, 128.03, 51.48; GC–MS *m/z* 202 (M⁺). Anal. Calc. for C₈H₁₁ClO₂Si: C, 47.40; H, 5.47. Found: C, 47.59; H, 5.74%.

3.4. One-pot synthesis of alkoxychlorosilanes from dihydrosilanes

A mixture of Hex₂SiH₂ (5.15 g, 25.7 mmol), EtOH (1.18 g, 25.7 mmol), and PdCl₂ (0.0087 g, 0.049 mmol) in 65 mL of benzene was stirred at room temperature and the reaction progress was monitored by GLC. After 24 h reaction, GLC analysis indicated that the starting Hex₂SiH₂ was wholly converted to Hex₂Si(OEt)H. To the resulting mixture was added CCl₄ (3.97 g, 25.8 mmol) and PdCl₂ (0.0105 g, 0.059 mmol), and the mixture was further stirred at room temperature for 24 h. After the resulting black precipitates were filtered, the

solvent was evaporated and the residue was fractionally distilled under reduced pressure to give Hex₂Si(OEt)Cl (5.67 g, 20.3 mmol; 79% yield).

The other one-pot synthesis of alkoxychlorosilanes from dihydrosilanes was carried out as above.

3.5. Bromination of alkoxyhydrosilanes

A mixture of Hex₂Si(OEt)H (1.13 g, 4.64 mmol), allyl bromide (0.57 g, 4.71 mmol), and PdCl₂ (0.0065 g, 0.037 mmol) in 10 mL of toluene was stirred at 60 °C for 6 h. The mixture was analyzed by GLC using *n*-eicosane as an internal standard as being Hex₂Si(OEt)Br in 88% yield. After filtration, followed by evaporation of the solvent, Hex₂Si(OEt)Br was separated from the residue by Kugel-rohr distillation. Its spectrometric analysis, however, indicated the existence of trace amounts of unidentified impurities. Attempted isolation of Hex₂Si(OEt)Br by repeated distillation failed, due to its high sensitivity toward moisture, and therefore, Hex₂Si(OEt)Br was subjected to the further reactions with nucleophiles after filtration followed by evaporation of the solvent. Data for Hex₂Si(OEt)Br: b.p. 95 °C, 1 mmHg (oven temperature); ¹H NMR δ 3.78 (q, *J* = 7.0 Hz, 2H), 1.45–1.18 (m, 19H), 0.94–0.85 (m, 10H); ¹³C NMR δ 59.64, 32.43, 31.36, 22.73, 22.50, 18.06, 14.06, 12.47; GC–MS *m/z* 322 (M⁺).

Preparation of Ph₂Si(OEt)Br from Ph₂Si(OEt)H was carried out as above: b.p. 100 °C, 1 mmHg (oven temperature on Kugel-rohr distillation); ¹H NMR δ 7.70 (dd, *J* = 7.9, 1.4 Hz, 4H), 7.46–7.38 (m, 6H), 3.94 (q, *J* = 7.0 Hz, 2H), 1.32 (t, *J* = 6.9 Hz, 3H); ¹³C NMR δ 134.82, 134.41, 131.05, 128.04, 60.44, 17.71; GC–MS *m/z* 306 (M⁺).

3.6. One-pot synthesis of Hex₂Si(OEt)Br from Hex₂SiH₂

A mixture of Hex₂SiH₂ (2.49 g, 12.4 mmol), EtOH (0.57 g, 12.4 mmol), and PdCl₂ (0.0028 g, 0.015 mmol) in 80 mL of benzene was stirred at room temperature and the reaction progress was monitored by GLC. After 24 h reaction, GLC analysis indicated that the starting Hex₂SiH₂ was wholly converted to Hex₂Si(OEt)H. To the resulting mixture was added allyl bromide (1.51 g, 12.5 mmol) and PdCl₂ (0.012 g, 0.067 mmol), and the mixture was further stirred at 50–60 °C for 8 h. The mixture was analyzed by GLC using *n*-eicosane as an internal standard as being Hex₂Si(OEt)Br in 91% yield. After filtration, followed by evaporation of the solvent, Hex₂Si(OEt)Br was separated from the residue by Kugel-rohr distillation. Its spectrometric analysis, however, indicated the existence of trace amounts of unidentified impurities.

3.7. Nucleophilic substitution of alkoxyhalosilanes

To a solution of Hex₂Si(OMe)Cl (1.91 g, 7.20 mmol) in 80 mL of ether was added dropwise 4.6 mL (7.2

mmol) of a 1.56 M *n*-BuLi–*n*-hexane solution at $-78\text{ }^{\circ}\text{C}$, and the resulting mixture was stirred at this temperature for 4 h. After the resulting lithium salt was filtered, the solvent was evaporated and the residue was fractionally distilled under reduced pressure by a Kugel-rohr distillation apparatus to give $\text{Hex}_2\text{Si}(\text{OMe})(n\text{-Bu})$ (1.77 g, 6.19 mmol; 86% yield): b.p. $95\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature); $^1\text{H NMR } \delta$ 3.42 (s, 3H), 1.30–1.26 (m, 20H), 0.88–0.85 (m, 9H), 0.60–0.56 (m, 6H); $^{13}\text{C NMR } \delta$ 50.88, 33.71, 31.87, 23.39, 26.93, 25.68, 22.92, 14.41, 14.20, 13.51, 13.22; GC–MS m/z 286 (M^+). Anal. Calc. for $\text{C}_{17}\text{H}_{38}\text{OSi}$: C, 71.25; H, 13.37. Found: C, 71.12; H, 13.37%.

Other reactions of alkoxyhalosilanes with nucleophiles were carried out as above. Data for $\text{Hex}_2\text{Si}(\text{OEt})(n\text{-Bu})$: b.p. $95\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 3.64 (q, $J = 7.0$ Hz, 2H), 1.30–1.26 (m, 20H), 1.17 (t, $J = 7.0$ Hz, 3H), 0.89–0.85 (m, 9H), 0.59–0.56 (m, 6H); $^{13}\text{C NMR } \delta$ 58.34, 33.37, 31.55, 26.63, 25.43, 23.14, 22.61, 18.64, 14.12, 13.76, 13.64, 13.35; GC–MS m/z 300 (M^+). Anal. Calc. for $\text{C}_{18}\text{H}_{40}\text{OSi}$: C, 71.92; H, 13.41. Found: C, 71.63; H, 13.27%. Data for $\text{Hex}_2\text{Si}(\text{OEt})(\text{CH}=\text{CH}_2)$: b.p. $85\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 6.12–6.00 (m, 2H, $\text{CH}=\text{}$ and $\text{CH}_2=\text{}$), 5.76 (dd, $J = 18.4, 6.0$ Hz, 1H, $\text{CH}_2=\text{}$), 3.67 (q, $J = 7.0$ Hz, 2H), 1.37–1.21 (m, 16H), 1.17 (t, $J = 7.0$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 6H), 0.65 (br t, $J = 7.2$ Hz, 4H); $^{13}\text{C NMR } \delta$ 135.68 ($\text{CH}_2=\text{}$), 133.24 ($\text{CH}=\text{}$), 58.34, 33.37, 31.55, 22.78, 22.42, 18.29, 13.87, 13.29; GC–MS m/z 270 (M^+). Anal. Calc. for $\text{C}_{16}\text{H}_{34}\text{OSi}$: C, 71.04; H, 12.67. Found: C, 71.03; H, 12.54%. Data for $\text{Hex}_2\text{Si}(\text{OEt})(\text{C}\equiv\text{CPh})$: b.p. $145\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 7.47 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.33–7.28 (m, 3H), 3.83 (q, $J = 6.9$ Hz, 2H), 1.46–1.22 (m, 19H), 0.88 (br t, $J = 7.0$ Hz, 6H), 0.74 (q, $J = 7.0$ Hz, 4H); $^{13}\text{C NMR } \delta$ 132.08, 128.68, 128.21, 122.83, 105.82 ($\equiv\text{CPh}$), 90.66 ($\equiv\text{CSi}$), 59.41, 32.90, 31.52, 22.95, 22.59, 18.32, 15.02, 14.12; GC–MS m/z 344 (M^+). Anal. Calc. for $\text{C}_{22}\text{H}_{36}\text{OSi}$: C, 76.68; H, 10.53. Found: C, 76.38; H, 10.62%. Data for $\text{Ph}_2\text{Si}(\text{OEt})(n\text{-Bu})$: b.p. $130\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 7.58 (dd, $J = 7.7, 1.7$ Hz, 4H), 7.40–7.36 (m, 6H), 3.75 (q, $J = 7.0$ Hz, 2H), 1.43–1.32 (m, 4H), 1.22–1.12 (m, 6H), 0.86 (t, $J = 7.0$ Hz, 2H); $^{13}\text{C NMR } \delta$ 135.46, 134.62, 129.63, 127.72, 59.20, 26.49, 25.13, 18.34, 13.68, 13.62; GC–MS m/z 284 (M^+). Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{OSi}$: C, 76.00;

H, 8.50. Found: C, 75.89; H, 8.62%. Data for $\text{Ph}_2\text{Si}(\text{OEt})(\text{CH}=\text{CH}_2)$: b.p. $95\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 7.62 (dd, $J = 7.7, 1.7$ Hz, 4H), 7.43–7.34 (m, 6H), 6.45 (dd, $J = 20.2, 14.9$ Hz, 1H, $\text{CH}=\text{}$), 6.24 (dd, $J = 14.9, 3.9$ Hz, 1H, $\text{CH}_2=\text{}$), 5.88 (d, $J = 20.2, 3.9$ Hz, 1H, $\text{CH}_2=\text{}$), 3.87 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR } \delta$ 136.84, 134.96, 134.38 ($\text{CH}_2=\text{}$), 133.63 ($\text{CH}=\text{}$), 129.91, 127.81, 59.54, 18.39; GC–MS m/z 254 (M^+). Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{OSi}$: C, 75.54; H, 7.13. Found: C, 75.64; H, 7.42%. Data for $\text{Ph}_2\text{Si}(\text{OEt})(\text{C}\equiv\text{CPh})$: b.p. $155\text{--}160\text{ }^{\circ}\text{C}$, 1 mmHg (oven temperature on Kugel-rohr distillation); $^1\text{H NMR } \delta$ 7.77 (dd, $J = 7.8, 1.8$ Hz, 4H, *o*-Ph–Si), 7.57 (dd, $J = 7.8, 1.8$ Hz, 2H, *o*-Ph–C), 7.44–7.33 (m, 9H), 3.94 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR } \delta$ 134.68, 133.87, 132.29, 130.32, 129.16, 128.30, 127.91, 122.34, 108.08 ($\equiv\text{CPh}$), 88.77 ($\equiv\text{CSi}$), 60.00, 18.17; GC–MS m/z 328 (M^+). Anal. Calc. for $\text{C}_{22}\text{H}_{20}\text{OSi}$: C, 80.44; H, 6.14. Found: C, 80.33; H, 6.18%.

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