Synthetic Methods

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Practical Conversion of Chlorosilanes into Alkoxysilanes without Generating HCl**

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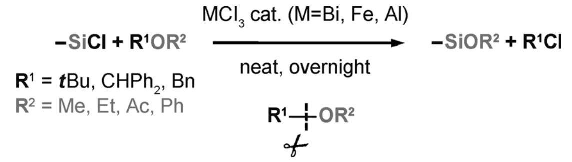
Alkoxysilanes are used as key starting materials in inorganic, organic, and materials chemistry for sol-gel processes,[1] surface modification (silane coupling agent),[2] protection of hydroxy groups (silyl ether),[3] and cross-coupling reactions (Hiyama coupling).[4] Various alkoxysilanes are industrially produced for diverse purposes.

The industrial and classical methods for synthesizing alkoxysilanes are based on the reaction of a chlorosilane and an alcohol; a reaction used since 1845.[5] However, the generation of HCl as a by-product has the potential to cause serious environmental and health problems. Gaseous HCl is not only very toxic but also decomposes alcohols, thereby lowering the yield of the reaction. A simple way to avoid the generation of HCl is to use a Lewis base as an acid scavenger. Lewis bases, such as pyridine and 2,6-lutidine, easily form their HCl salts and make the reaction system neutral. However, the required amount of such an acid scavenger is equimolar to that of generated HCl, thus making this approach not feasible for industrial processes. Moreover, filtration is required to remove these HCl salts. These steps are laborious because alkoxysilanes are moisture sensitive. HCl generation can be avoided through a two-step reaction; reduction of the chlorosilane to the hydrosilane and subsequent alkoxylation with alcohol. However, this process may cause hazards arising from highly reactive reducing agents ($LiAlH_4$ etc.) and the release of H_2. Much effort has been devoted to exploring reagents other than alcohols for the alkoxylation of chlorosilanes. Such reagents are alkali-metal alkoxides (MOR: M = Li, Na, K; R = Me, Et)[6] and trialkyl orthoformates ($HC(OR)_3$),[7] for example. However, they themselves are unstable to moisture, and the latter generates several by-products, including alkyl formates (HCOOR) and alkyl chlorides (RCl), in alkoxylation reactions. Thus, these reagents have rarely been used in experimental and industrial processes to date, therefore making a truly practical synthetic procedure that does not involve hazardous substances desirable.

Herein we report the practical synthesis of alkoxysilanes directly from chlorosilanes (Scheme 1). Our method uses unsymmetrical ethers instead of alcohols. Unsymmetrical ethers (R^1OR^2), such as MTBE (methyl *tert*-butyl ether: $R^1 = t$Bu, $R^2 =$ Me) and ETBE (ethyl *tert*-butyl ether: $R^1 = t$Bu, $R^2 =$ Et), can be used as the source of methoxy and ethoxy groups, respectively. They are relatively safe, stable, and easy to handle relative to other agents (MOR or $HC(OR)_3$) used for this purpose, and this is assured by their extensive usage as an additive for gasoline. Although the representative by-product, *tert*-butyl chloride ($R^1 = t$Bu) has to be captured and should not be released into the environment, it will be less problematic because the by-product is easily distilled (b.p. 52 °C) and has no serious toxicity. In addition, alkyl chlorides (R^1Cl) are useful as reactants for various organic reactions, including Grignard reactions.



Scheme 1. Synthesis of alkoxysilanes and acetoxysilanes from chlorosilanes.

The use of unsymmetrical ethers in the present reaction scheme has led to the synthesis of alkoxysilane monomers through selective cleavage of C–O bond. This idea has been inspired by previous studies on nonhydrolytic sol-gel process which uses symmetrical ethers.[8] Symmetrical ethers are known to react with chlorosilanes in the presence of Lewis acids to form silica. The cleavage of the C–O bond strongly depends upon the stability of the resulting carbocations in the case of symmetrical ethers[8] and alkoxysilanes.[8–10] Nonhydrolytic sol-gel processes are applicable not only to silica but also to other inorganic oxides. Though alkoxysilanes are formed in situ, they are intermediates and alkoxysilane

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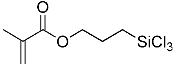
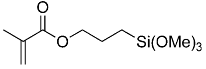
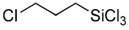
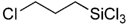
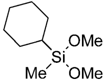
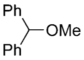
monomers are not isolated. The cleavage of two identical C–O bonds in one symmetrical ether molecule occurs under the same reaction conditions. In contrast, we have chosen unsymmetrical ethers for the selective synthesis of alkoxysilane monomers by utilizing the difference in the stabilities of resulting carbocations (R^{1+} and R^{2+}). To the best of our knowledge, this selective cleavage of a C–O bond in an unsymmetrical ether using a chlorosilane and Lewis acid is realized for the first time. The formation of the Si–O–C bond with unsymmetrical ethers was reported by Jung et al., as the dealkylation reaction of an unsymmetrical ether with iodotrimethylsilane (Me_3SiI).[11,12] The study was aimed at converting ethers into silyl ethers for subsequent removal of the silyl group to reveal the alcohol. Although iodotrimethylsilane was synthesized by several methods,[11–13] iodosilanes having practical organosilyl groups are limited.[13,14] Iodosilanes are moisture sensitive in contrast to chlorosilanes.[14] Therefore, the use of iodosilanes is fairly limited for the preparation of alkoxysilanes.

We examined the reactions of various organochlorosilanes with MTBE by using a $BiCl_3$ catalyst (entries 1–10, Table 1). The formation of alkoxysilanes was confirmed by ^1H, ^{13}C, and ^{29}Si NMR measurements (see the Supporting Information). Each corresponding alkoxysilane was obtained in a satisfactory yield (75–97 %). In addition, the presence of approximately equimolecular amounts of *tert*-butyl chloride (R^1Cl) and -SiOMe groups was proven by ^1H and ^{13}C NMR spectroscopy; thus confirming that the reaction proceeds without generating HCl.

Table 1: Syntheses of alkoxysilanes and acetoxysilanes from chlorosilanes.[a]

Entry	Chlorosilane	R^1OR^2	Product	Yield [%][b]
1	$PhSiCl_3$	*t*BuOMe	$PhSi(OMe)_3$	97
2	$CH_2{=}CHSiCl_3$	*t*BuOMe	$CH_2{=}CHSi(OMe)_3$	95
3	$CH_3(CH_2)_{11}SiCl_3$	*t*BuOMe	$CH_3(CH_2)_{11}Si(OMe)_3$	91
4		*t*BuOMe		91
5	$SiCl_4$	*t*BuOMe	$Si(OMe)_4$	85
6	$SiCl_4$	*t*BuOMe	$ClSi(OMe)_3$	80
7		*t*BuOMe		92
8	Me_2SiCl_2	*t*BuOMe	$Me_2Si(OMe)_2$	85
9		*t*BuOMe		86
10	Me_3SiCl	*t*BuOMe	$Me_3Si(OMe)$	75
11	$PhSiCl_3$		$PhSi(OMe)_3$	56
12	$PhSiCl_3$	BnOMe	$PhSi(OMe)_3$	0
13[d]	$PhSiCl_3$	BnOMe	$PhSi(OMe)_3$	57
14[e]	$MeSiCl_3$	BnOPh	$MeSi(OPh)_3$	63
15	$PhSiCl_3$	*t*BuOEt	$PhSi(OEt)_3$	90
16	$CH_2{=}CHSiCl_3$	*t*BuOAc	$CH_2{=}CHSi(OAc)_3$	88

[a] Reactions were conducted overnight under an N_2 atmosphere at RT. A slight excess (1.1–1.3-fold excess to the number of -SiCl groups of chlorosilane) of the unsymmetrical ether (R^1OR^2) or ester (entry 16) was added. NMR measurements were performed without further purification. All the ^1H, ^{13}C, ^{29}Si NMR data are shown in the Supporting Information (MS data for entry 14 are also included). [b] Determined by ^{29}Si NMR spectroscopy. A trace amount of $[Cr(acac)_3]$ (acac = acetylacetonate) was added to obtain quantitative data. The repetition time between each pulse was 10 s (see the Supporting Information for the details.) [c] 3 equiv R^1OR^2 relative to $SiCl_4$ was used. [d] Reaction was conducted at 80 °C. [e] Reaction was conducted at 60 °C.

In addition to alkoxysilanes, chloroalkoxysilanes are also valuable as they can be utilized for the synthesis of other organoalkoxysilanes and organoalkoxysiloxane oligomers for nano- and mesostructured silica-based hybrids.[9,15] They can be synthesized by our procedure with good selectivity by just adding a controlled amount of an unsymmetrical ether without any special apparatus (entry 6, Table 1).

Functional groups other than the *tert*-butyl group for R^1 were also investigated. The diphenylmethyl ($-CHPh_2$) group (entry 11, Table 1) behaves similarly to the *tert*-butyl group as seen in our previous study on the siloxane formation.[9] In contrast, no C–O bond cleavage was observed with benzyl ethers at room temperature (entry 12, Table 1). Heating is required for the reactions using benzyl ethers (entries 13 and 14, Table 1).

This procedure was also applied to other alkoxy and acetoxy groups to estimate the scope with respect to R^2 (entries 14–16, Table 1). Other ethers and esters, such as ETBE ($R^1 = t\mathrm{Bu}$, $R^2 = \mathrm{Et}$), benzyl phenyl ether ($R^1 = \mathrm{Bn}$, $R^2 = \mathrm{Ph}$), and *tert*-butyl acetate ($R^1 = t\mathrm{Bu}$, $R^2 = \mathrm{Ac}$) were examined instead of MTBE, and the corresponding ethoxy-, phenoxy-, and acetoxysilanes were successfully obtained.

Compared to the conventional procedures starting with an alcohol, the result is dramatically different especially in methoxylation of cyclohexyl(methyl)dichlorosilane (entry 9, Table 1). The ^{29}Si NMR spectra of the products after methoxylation of cyclohexyl(methyl)dichlorosilane using our method (Figure 1 a) and the conventional procedure with an alcohol (Figure 1 b) are shown; the same apparatus and reaction conditions were used. The spectrum (Figure 1 a) shows the main signal at $\delta = -3.6$ ppm, which indicates the formation of

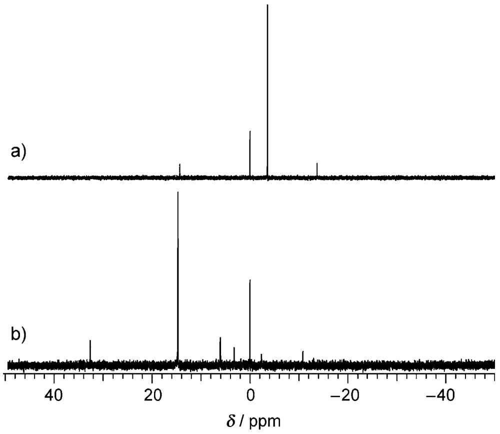


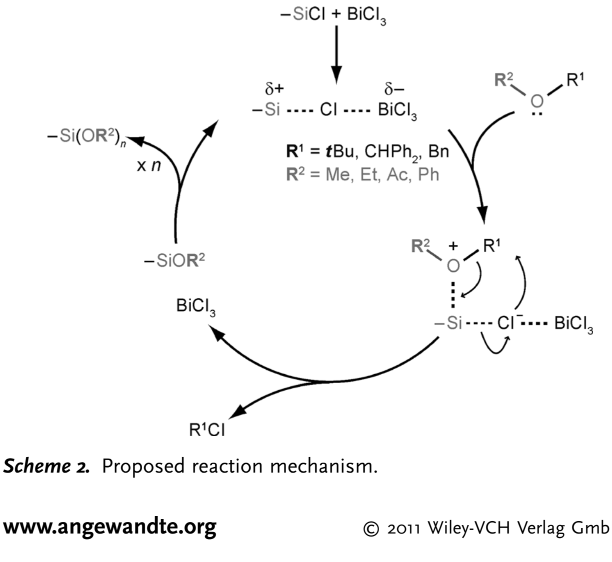
Figure 1. ^{29}Si NMR spectra of methoxylated cyclohexyl(methyl)dichlorosilane using a) our method (see entry 9 in Table 1) and b) the conventional procedure for alcohols. The signal at $\delta = 32.6$ ppm is due to unreacted cyclohexyl(methyl)dichlorosilane. The signals at $\delta = 14.3$ and -13.7 ppm are tentatively assigned as cyclo-hexyl(methyl)(methoxy)chlorosilane and 1,3-dicyclohexyl-1,3-dimethyl-1,3-dimethoxydisiloxane, respectively.

cyclohexyl(methyl)dimethoxysilane in high selectivity. In contrast, the same signal does not appear in the second spectrum (Figure 1b), while other compounds are present (see the caption of Figure 1). Cyclohexyl(methyl)dichlorosilane has low reactivity with alcohols, and competing side reactions (decomposition of alcohol to form alkyl chloride and water) arising from HCl are inevitable. In fact, the conventional procedure involving alcohols requires careful removal of HCl to produce cyclohexyl(methyl)dimethoxysilane and avoid side-reactions. However, the procedure reported herein requires no special attention.

The necessity of a catalyst was investigated by the reaction with MTBE and $SiCl_4$ without $BiCl_3$ (see entries 5 and 6, Table 1). $SiCl_4$ was chosen as the reactant because its Lewis acidity is expected to be the strongest among the chlorosilanes as a result of the presence of four electron-withdrawing chlorine atoms attached to Si. The ^{29}Si NMR spectrum of the above-metioned control experiment (see Figure S1 in the Supporting Information) only shows a signal for $SiCl_4$, even after a longer reaction time (3 days) at room temperature; that is, -SiCl groups are not changed into -SiOMe ($-SiOR^2$) groups at all. These results imply the necessity of a Lewis acid catalyst in this procedure. The catalyst of the reaction is not limited to $BiCl_3$, as other Lewis acids, such as $FeCl_3$ and $AlCl_3$ also work (see Figure S2). $FeCl_3$ behaves similarly to $BiCl_3$, and $AlCl_3$ catalyzes the reaction, but at a much slower rate. The differences in the efficiency among the Lewis acid catalysts will be reported elsewhere.

A plausible reaction mechanism is shown in Scheme 2. This reaction involves three reaction steps.[9,10,16,17] First, $BiCl_3$ activates the Si–Cl bond. Then nucleophilic attack of the oxygen atom onto Si occurs to form a silyloxonium cation as an intermediate. A cation rearrangement is then driven by the formation of a stable carbocation to form a $Si{-}OR^2$ bond. At the same time, Cl^- attacks R^{1+} to form R^1Cl. This reaction is repeated to form the corresponding alkoxysilane.

Another possibility for the reaction pathway is the formation of an alcohol by the cleavage of a C–O bond and then subsequent reaction with the chlorosilane in a fashion that is similar to that in the conventional procedure. Cleavage of the C–O bond with $BiCl_3$ alone was previously reported for trityl ($-CPh_3$) ethers.[18] Both trityl and *tert*-butyl groups are known to form stable carbocations. However, in our procedure, the unsymmetrical ether was observed in the NMR spectra for all the experiments and no signals that were assignable to alcohols were detected. Additionally, the ^{29}Si NMR spectra (Figure 1) show the difference between our reaction and the classical method. If alcohols were initially formed the reaction with the chlorosilane would form HCl, which decomposes alcohols to form alkyl chloride and water; therefore we would expect the spectra of the product to be similar to that for the classical method (Figure 1b). As this is not the case, our reaction does not involve alcohols in contrast to the classical method.



Scheme 2. Proposed reaction mechanism.

In the procedure presented herein, alkoxysilane dimers are unexpectedly obtained according to the ^{29}Si NMR spectra (see the Supporting Information). These by-products appear in small amounts and probably arise from the cleavage of a $R^1O{-}R^2$ bond to form $-SiOR^1$ groups, and subsequent formation of a siloxane bond with another chlorosilane.[9] Formation of $Si{-}OR^1$ ($R^1 = t$Bu) as an intermediate is suggested because the signals around $\delta = 31$–30 ppm ($-OC(CH_3)_3$) were observed in the ^{13}C NMR spectra for entries 2, 6, 8, 10, and 16 in Table 1 (see the Supporting Information). To additionally improve the selectivity of targeted alkoxysilane monomers, the investigation of more appropriate catalysts and reaction conditions will be continued.

In conclusion, we have demonstrated the facile and efficient procedure for the selective synthesis of various alkoxysilanes without generating HCl. This procedure is profitable because of its mild reaction conditions, easy-to-handle reagents, and production of a minimum number of by-products. The present results make the synthesis of a wide variety of alkoxysilanes easier and cost-effective in both academic and industrial fields.

Experimental Section

A typical synthetic procedure is as follows (entry 1, Table 1; synthesis of phenyltrimethoxysilane). Phenyltrichlorosilane (1.6 mL, 10 mmol) was added to a mixture of $BiCl_3$ (32 mg, 0.1 mmol) and MTBE (3.9 mL, 33 mmol) in a 30 mL schlenk flask at 0°C. The molar ratio was $PhSiCl_3/MTBE/BiCl_3 = 1{:}3.3{:}0.01$. The mixture was stirred overnight at RT. The progress of the reaction was estimated by NMR measurements without any further purification.

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