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The Carbon–Silicon Bond Cleavage of Organosilicon Compounds in Supercritical Water

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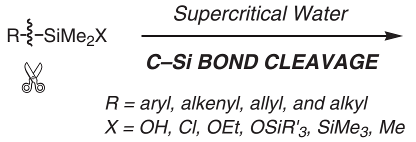
Arylsilanes, alkenylsilanes, allylic silanes, and alkylsilanes were found to undergo extremely facile and rapid C–Si bond cleavage in supercritical water. Rapid C–Si bond cleavage occurred even with robust unactivated tetraalkylsilanes. The control experiments revealed the dramatic difference between the supercritical and subcritical conditions, and that between supercritical water and supercritical methanol, attesting to a unique reactivity of supercritical water in C–Si bond cleavage. It was also found that acids, such as HCl, HBr, and H_2SO_4, promote C–Si bond cleavage in supercritical water.

In recent years, considerable attention has been directed toward a new medium for chemical synthesis (reaction and separation) for many reasons.[1] For example, the execution of organic reactions in water (or aqueous media)[2] has received particular attention by organic chemists, since it allows "green" or environmentally benign chemical processes.[3] In addition, the exploitation of unique properties of water, such as hydrophobic effects, hydrogen-bonding interactions, and high polarity, has been a recent topic of interest, and many interesting chemical reactions in water have been continuously reported very recently.[4,5]

Supercritical water (scH_2O, the critical temperature: 374 °C, the critical pressure: 22.1 MPa) has been attracting increasing attention because of its unique physical and chemical properties, which are very different from those of ambient water.[6] For example, because the dielectric constant is much lower, many organic compounds are miscible in scH_2O. Furthermore, the ion-dissociation constant of water initially increases as the temperature rises, and drops dramatically at the critical point under a constant-pressure condition.

Because of its harsh conditions and miscibility of organic compounds and oxygen, scH_2O has tended to be used as a medium for the oxidative treatment of organic waste, or for the degradation of waste synthetic polymers, vegetable oils, and biomass. Recently, however, many researchers have set out to use scH_2O as a medium of chemical synthesis. Many examples have proved that selective transformation and bond formation are plausible instead of complete decomposition of organic compounds. These include the Diels–Alder reaction,[7] Friedel–Crafts alkylation,[8] Beckmann and pinacol rearrangements,[9] ester hydrolysis,[10] and Pd-catalyzed Mizoroki–Heck reaction.[11]

Organosilicon compounds have been extensively utilized in modern organic synthesis.[12] Taking the high oxophilicity of silicon into account, water would be expected not only as a new reaction medium, but also as a Lewis basic donor (activator) for silicon under supercritical conditions. Our continuing interests in silicon-based organic synthesis[13] and in aqueous organic reactions[14] have led us to explore the feasibility of silicon-based organic synthesis in scH_2O, which has not been reported to date. During the course of this study, we discovered an extremely facile C–Si bond cleavage of organosilicon compounds in scH_2O for the first time, which serves as a starting point toward the development of silicon-based organic synthesis in scH_2O (Eq. 1).[15]



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In this paper, we report on the full details of this study.

Results and Discussion

Examined Organosilicon Compounds. In this study, a wide array of organosilicon compounds with different structural and electronic properties was examined. They are shown in Fig. 1. We began our research by examining arylsilanes, alkenysilanes, and allylic silanes, which usually exhibit high reactivity toward C–Si bond cleavage. As for more robust alkylsilanes, compounds with heteroatom on silicon were initially examined. Most challenging tetraalkylsilanes were examined in detail, including the effect of additives.

Apparatus. Reactions of organosilicon compounds in scH_2O were carried out, as shown in Fig. 2 (see Experimental Section for details). As usual, the reactions could be conducted directly in a stainless-steel container (SUS316), submerged in a dissolved salt bath ($NaNO_2/KNO_3$) of high temperature (method A). However, any positive or negative effect of the stainless-steel reactor (metallic surface) cannot be excluded

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by using this method.[16] Therefore, most of the reactions in this study (except for reactions using **3** and **4**) were performed in a sealed quartz tube placed in a stainless-steel container (method B).[17] To avoid breakage of the quartz ampoule due to a pressure increase, a calculated amount of water was added to the stainless tube to maintain a balanced pressure. The temperature was monitored by a thermocouple inserted through the top end of the stainless-tube container. The stainless tube was submerged in a dissolved salt bath ($NaNO_2/KNO_3$), whose temperature was controlled. After a specified time, the tube was removed and cooled in a water bath. The reaction products were analyzed by standard methods, such as capillary GC, GC–MS, and NMR. Although we have never experienced an accident, all reactions in supercritical water should be performed with great care due to the high-temperature/pressure conditions.

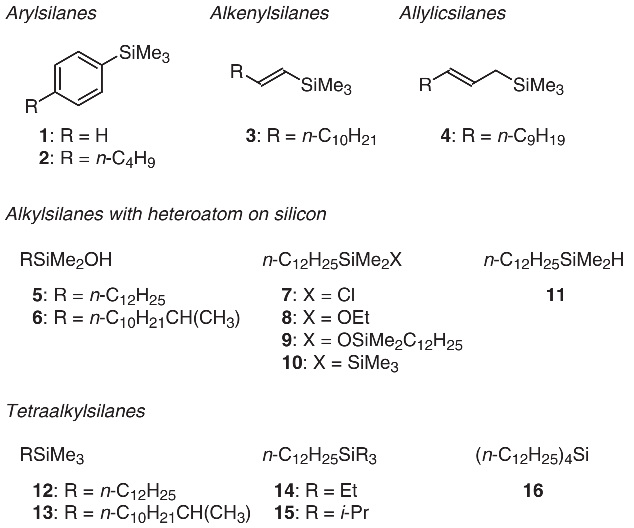
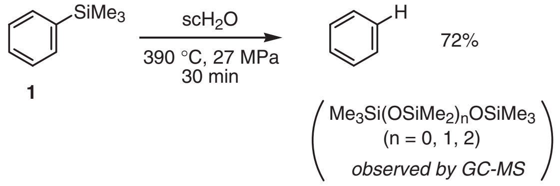


Fig. 1. Examined organosilicon compounds in this study.

Arylsilanes. Electrophilic cleavage of C–Si bonds in arylsilanes has been extensively utilized in organic synthesis because a coming electrophile always occupies the position where the silyl group has been attached.[18] This *ipso* substitution is extremely useful in the regioselective carbon–carbon and carbon–heteroatom bond formations at aromatic rings. It is generally assumed that proton transfer, rather than desilylation, is the rate-determining step of this reaction.[19] Thus, we began our research by subjecting arylsilanes to scH_2O. When trimethylphenylsilane (**1**) was subjected to scH_2O, C–Si bond cleavage occurred within 30 min at 390 °C to give benzene in 72% yield (Eq. 2).



(2)

As judged by GC–MS analysis, siloxanes $Me_3Si(OSiMe_2)_n$-$OSiMe_3$ ($n = 0$–2) were found in the reaction mixture under these conditions. Similarly, (4-butylphenyl)trimethylsilane (**2**) also underwent rapid C–Si bond cleavage within 30 min at 390 °C to give butylbenzene in 91% yield (Eq. 3).

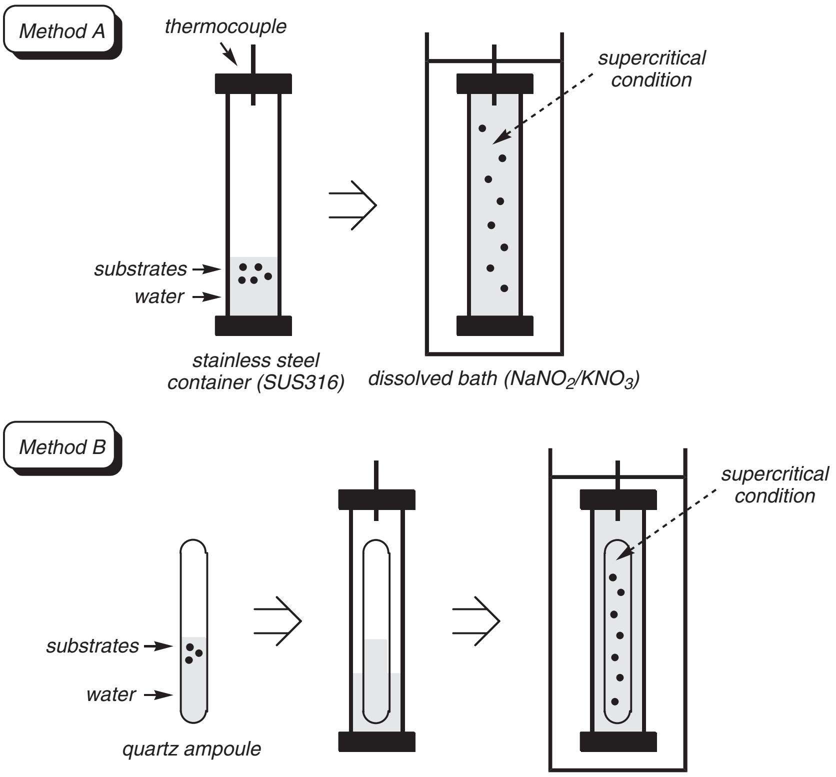
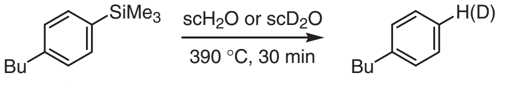


Fig. 2. Methods for the reactions of organosilicon compounds in supercritical water.

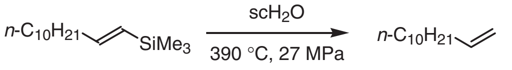


2 (3)

scH₂O: 91% yield
scD₂O: 74% yield, >95% D

As expected, the use of D_2O resulted in the introduction of deuterium (>95% D) at the position where the silyl group was previously bonded.[18] Though efficient C–Si bond cleavage occurred under scH_2O, supercritical conditions are not necessarily required for the C–Si bond cleavage for these reactive organosilicon compounds. For example, **1** did undergo C–Si bond cleavage in subcritical water (350 °C).

Alkenylsilanes. Encouraged by these promising results, we next examined alkenylsilanes. The reactions were conducted directly in a stainless-steel container (method A in Fig. 2), because an unavoidable explosion occurs during breakage of the quartz ampoule with method B. When alkenylsilane (**3**) was subjected to scH_2O (390 °C, 30 min), efficient C–Si bond cleavage occurred to give a mixture of dodecenes in 71% yield (Eq. 4).

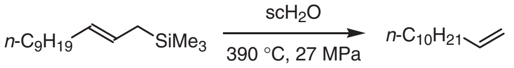


3 + other dodecenes (4)

reaction time	yield	1-dodecene/other dodecenes
1 min	31%	84/16
5 min	67%	19/81
30 min	71%	6/94

The expected 1-dodecence was obtained only in small amounts. The initial desilylation product (1-dodecene) seemed to isomerize into thermodynamically more stable inner alkenes under the reaction conditions. Indeed, isomerization into inner alkenes was observed when 1-dodecene was subjected to scH_2O at 390 °C (ratio of 1-dodecene and other dodecenes: 76/24 after 5 min; 4/96 after 180 min). In line with these results, when the reactions of **3** were performed in a shorter reaction time (5 min and 1 min), the ratio of 1-dodecene and other dodecenes increased to 19/81 and 84/16, respectively (Eq. 4).

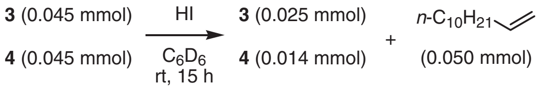
Allylic Silanes. Allylic silanes, another class of reactive organosilicon compounds, were also investigated. Because the reaction using these substrates also resulted in an unavoidable explosion during breakage of the quartz ampoule with method B, the reactions were conducted directly in a stainless-steel container (method A). Similarly to alkenylsilane **3**, allylic silane **4** also underwent rapid C–Si bond cleavage in scH_2O (Eq. 5).



4 + other dodecenes (5)

reaction time	yield	1-dodecene/other dodecenes
5 min	55%	>95/5
30 min	79%	83/17

In this case, 1-dodecene was found to be a major product (83% selectivity), even after 30 min. When the reaction time was shortened to 5 min, the ratio of 1-dodecene and other dodecenes increased to >95/5. This is in a sharp contrast with the reaction of **3** in scH_2O after 5 min (19/81; Eq. 4). Quite interestingly, the competitive reaction of **3** and **4** indicated a faster C–Si bond cleavage of **3** in scH_2O, although the opposite reactivity order is generally observed in the reaction with electrophiles.[20] Indeed, when we subjected a 1:1 mixture of **3** and **4** into a benzene solution of HI at room temperature,[21] allylic silane **4** underwent protodesilylation faster than alkenylsilane **3** (Eq. 6),



(6)

which clearly implicates that **4** is more reactive than **3** under typical desilylation conditions. Under these conditions, the isomerization of 1-dodecene to other dodecenes was not observed. Therefore, the results demonstrated herein imply a unique desilylation in scH_2O, though the elucidation of mechanistic origin must await further investigations.

Alkylsilanes with Heteroatom on Silicon. Having established the rapid C–Si bond cleavage of somewhat reactive organosilicon compounds (arylsilanes, alkenylsilanes, and allylic silanes), we next examined the reactions of alkylsilanes, which are known to be much less reactive toward C–Si bond cleavage than the organosilanes mentioned before.[12] Thus, we began by investigating alkylsilanes having a heteroatom on silicon, since such a heteroatom allows the activation of alkylsilanes by a nucleophile, such as a fluoride ion, to achieve otherwise difficult C–Si bond functionalizations.[22]

Alkylsilanol **5** was our first choice in this investigation (Table 1). Under the supercritical conditions (380 °C, 3 h), alkylsilanol **5** underwent efficient C–Si bond cleavage in water, giving dodecane in 68% yield (entry 1). Raising the temperature (390–410 °C) had little effect on the product yield (entries 2–4). However, the desilylation was extremely sluggish at 350 °C (subcritical conditions) and the corresponding siloxane **9** was obtained in 30% yield (entry 5). When the reaction time was shortened (20, 10, and 5 min), the conversion of **5** was decreased (entries 6–8). In the reaction mixture of these reactions, siloxane **9** was obtained in considerable yields (3–32%). The use of D_2O in place of H_2O also resulted in C–Si bond cleavage at 390 °C with the introduction of deuterium (>95% D) at the position where the silyl group had been previously bonded (entry 9). Interestingly, it was found that the addition of HCl (1.0 equiv to **5**) had a beneficial effect on the C–Si bond cleavage, giving dodecane in 88% yield at 390 °C (entry 10). However, the addition of excess HCl (2.0 equiv to **5**) did not cause a further increase in the yield (entry 11). The addition of HCl also had a dramatic enhancement of C–Si bond cleavage in subcritical water (350 °C), giving dodecane in 93% yield (entry 12). Moreover, in addition to HCl, NaOH was also found to promote the C–Si bond cleavage of **5** in scH_2O (entry 13). However, the addition of NaCl had little effect on the product yield (entry 14). With these interesting C–Si bond cleavage reactions of alkylsilanol **5** in hand, we next examined the reaction in supercritical methanol. When **5** was subjected to supercritical methanol, no C–Si bond cleavage occurred, and only the corresponding methoxysilane was obtained in 53% yield (entry 15).

Table 1. C–Si Bond Cleavage of Alkylsilanol **5** under Various Conditions

$$\underset{\mathbf{5}}{n\text{-}C_{12}H_{25}SiMe_2OH} \longrightarrow n\text{-}C_{12}H_{26}$$

Entry	Medium	*T*/°C	Time/min	Additive (equiv)	Conv/%[a]	Yield/%[a]
1	H_2O	380	180	—	100	68
2	H_2O	390	180	—	100	68
3	H_2O	400	180	—	100	67
4	H_2O	410	180	—	100	66
5	H_2O	350	180	—	70	11[b]
6	H_2O	390	20	—	83	30[c]
7	H_2O	390	10	—	68	20[d]
8	H_2O	390	5	—	55	12[e]
9	D_2O	390	180	—	100	54[f]
10	H_2O	390	180	HCl (1.0)	100	88
11	H_2O	390	180	HCl (2.0)	100	88
12	H_2O	350	180	HCl (1.0)	100	93
13	H_2O	390	180	NaOH (1.0)	100	85
14	H_2O	390	180	NaCl (1.0)	100	64
15	MeOH	390	180	—	100	0[g]

a) Determined by GC analysis using tetradecane as an internal standard. b) **9** was obtained in 30%. c) **9** was obtained in 3%. d) **9** was obtained in 16%. e) **9** was obtained in 32%. f) Deuterium incorporation was estimated to be greater than 95% as judged by NMR analysis. g) $C_{12}H_{25}SiMe_2OMe$ was obtained in 53%.

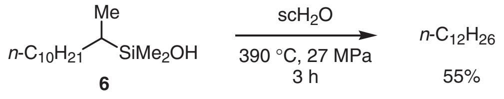
Table 2. C–Si Bond Cleavage of Alkylsilanes with Heteroatom on Silicon

$$n\text{-}C_{12}H_{25}SiMe_2X \xrightarrow[\text{390 °C, 3 h}]{scH_2O} n\text{-}C_{12}H_{26}$$

Entry	X	Additive (equiv)	Conv/%[a]	Yield/%[a]
1	Cl (**7**)	—	100	89
2	OEt (**8**)	—	100	23
3	OEt (**8**)	HCl (1.0)	100	72
4	$OSiMe_2C_{12}H_{25}$ (**9**)	—	100	46
5	$OSiMe_2C_{12}H_{25}$ (**9**)	HCl (1.0)	100	88
6	$SiMe_3$ (**10**)	—	100	56
7	$SiMe_3$ (**10**)	HCl (1.0)	100	91

a) Determined by GC analysis using tetradecane as an internal standard.

In addition to the primary alkyl–silyl bond, a secondary alkyl–silyl bond of alkylsilanol was also cleaved in scH_2O. Thus, when **6** was subjected in scH_2O (390 °C, 27 MPa) for 3 h, a desilylation product (dodecane) was obtained in 55% yield (Eq. 7).



(7)

The efficiency was somewhat lower than the corresponding primary alkyl–silyl bond (Table 1, entry 2).

Having established the efficient C–Si bond cleavage of alkylsilanols in scH_2O, we subsequently examined other alkylsilanes with heteroatom on silicon (Table 2). All reactions were carried out at 390 °C for 3 h. The reaction using chlorosilane **7** gave dodecane in 89% yield (entry 1). The higher yield, as compared to that with the corresponding alkylsilanol **5** (Table 1, entry 2), may be due to the effect of HCl generated in situ. Compared with alkylsilanol and chlorosilane, the desilylation was less efficient when ethoxysilane **8**, siloxane **9**, and disilane **10** were used (entries 2, 4, and 6). However, the addition of HCl gave rise to higher yields of the desilylation products (entries 3, 5, and 7).

During these studies, we found an interesting reactivity of alkylsilane **11** that has a Si–H bond in scH_2O. When alkylsilane **11** was subjected to scH_2O (390 °C, 30 min), alkylsilanol **5** (50%) and its dimer **9** (18%) were found in the reaction mixture together with dodecane (Eq. 8).

$$\underset{\mathbf{11}}{n\text{-}C_{12}H_{25}SiMe_2H} \xrightarrow[\substack{\text{390 °C, 27 MPa}\\ \text{30 min}}]{scH_2O} \begin{array}{ll} n\text{-}C_{12}H_{26} & (12\%) \\ n\text{-}C_{12}H_{25}SiMe_2OH & \mathbf{5}\ (50\%) \\ (n\text{-}C_{12}H_{25}SiMe_2)_2O & \mathbf{9}\ (18\%) \end{array} \qquad (8)$$

When the reaction was carried out in 380 °C for 1 h, alkylsilanol **5** became the exclusive product (Eq. 9).

$$\underset{\mathbf{11}}{n\text{-}C_{12}H_{25}SiMe_2H} \xrightarrow[\substack{\text{380 °C, 24 MPa}\\ \text{1 h}}]{scH_2O} \underset{\mathbf{5}\ (72\%)}{n\text{-}C_{12}H_{25}SiMe_2OH} \qquad (9)$$

Since the reactions were performed under oxygen-free conditions (the quartz ampoule was flame sealed after three freeze–pump–thaw cycles), the present transformation most likely proceeded through hydrolysis of the Si–H bond.[23] This may be an interesting alternative to the existing Si–H to Si–OH transformations, since it does not require any oxidants[24] or metal catalysts.[25] It is noteworthy that this method does not suffer from the production of disiloxane, which has often been a bane in the existing synthetic methods of silanol.

Tetraalkylsilanes. The successful desilylation of functionalized alkylsilanes finally led us to the ultimate challenge, the C–Si bond cleavage of unactivated tetraalkylsilanes. It has been stated by Armitage in his comprehensive review that "Tetraalkylsilanes are remarkably stable compounds. The silicon–carbon bond is strong and almost non-polar. It is therefore only broken under the most vigorous conditions, unless assisted by an alkyl group possessing an activating substituent suitably placed."[26] Therefore, the cleavage of the C–Si bonds in robust tetraalkylsilanes has been a subject of great interest in organic chemistry. Previously, strong acids,[27–29] bases,[30,31] or metal salts[32–43] were required to accomplish the C–Si bond cleavage of unactivated tetraalkylsilanes.[44,45]

Beyond our imagination, this transformation was found to be extremely rapid in scH_2O (Table 3). Primary alkyltrimethylsilane **12** underwent expeditious C–Si bond cleavage at 390 °C within 30 min giving dodecane in 72% yield (entry 1).[46] By adding HCl, we increased the yield to 88% (entry 2). The desilylation was extremely inefficient in subcritical water (entry 3), or entirely sluggish in refluxing HCl/H_2O (entries 4 and 5) or in supercritical methanol (entry 6).

The effect of substituents on silicon was subsequently examined (Table 4). The desilylation of secondary alkylsilane **13** was less efficient (1%) at 390 °C (entry 3). This may be due to the steric hindrance around the silicon atom. The same tendency was observed when Et_3Si and i-Pr_3Si groups were attached in place of the Me_3Si group (entries 5 and 7). Such a considerable reactivity difference may be useful for selective desilylation from a compound bearing several different silyl groups. However, in all cases, the addition of HCl again accelerated the cleavage of these sterically hindered C–Si bonds, and the reactions completed within 30 min (entries 4, 6, and 8).

When tetra(1-dodecyl)silane (**16**) was used as a substrate, 368% of 1-dodecane was formed under the influence of HCl (1.0 equiv) in scH_2O (390 °C, 30 min) (Eq. 10).

$$\underset{\textbf{16}}{(n\text{-}C_{12}H_{25})_4Si} \xrightarrow[\substack{390\ ^\circ C,\ 0.5\ h \\ 1\ \text{equiv HCl}}]{scH_2O} \underset{368\%}{n\text{-}C_{12}H_{26}} \qquad (10)$$

This result unambiguously verifies that all C–Si bonds of tetraalkylsilanes are cleaved in scH_2O.

We next examined the effect of several other additives in the reaction of tetraalkylsilanes **14** in scH_2O (Table 5). As already mentioned, the addition of 1.0 equiv of HCl gave rise to the production of dodecane in 79% yield (entry 2). Reducing the amount (0.1 equiv) of HCl resulted in a somewhat lower yield of dodecane (65%, entry 3). Other acids, such as HBr and H_2SO_4, also promoted C–Si bond cleavage, giving dodecane in high yields (93% and 75% yields, respectively). Inter-

Table 3. C–Si Bond Cleavage of Tetraalkylsilane **12** under Various Conditions

$$\underset{\textbf{12}}{n\text{-}C_{12}H_{25}SiMe_3} \longrightarrow n\text{-}C_{12}H_{26}$$

Entry	Medium	T/°C	Time/h	Additive (equiv)	Conv/%[a)]	Yield/%[a)]
1	H_2O	390	0.5	—	100	72
2	H_2O	390	0.5	HCl (1.0)	100	88
3	H_2O	350	0.5	—	35	11[b)]
4	H_2O	110	14	—	3	0
5	H_2O	110	14	HCl (1.0)	4	0
6	MeOH	390	0.5	—	20	1

a) Determined by GC analysis using tetradecane as an internal standard. b) **5** was obtained in 9%.

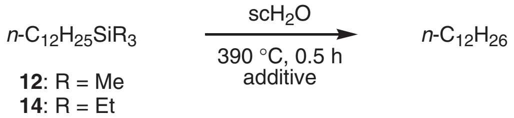
Table 4. Effect of Substituents on Silicon

$$C_{12}H_{25}SiR_3 \xrightarrow[390\ ^\circ C,\ 0.5\ h]{scH_2O} C_{12}H_{26}$$

Entry	Silane	Additive (equiv)	Conv/%[a)]	Yield/%[a)]
1	n-$C_{12}H_{25}SiMe_3$ (**12**)	—	100	72
2	**12**	HCl (1.0)	100	88
3	n-$C_{10}H_{21}CH(CH_3)SiMe_3$ (**13**)	—	8	1
4	**13**	HCl (1.0)	100	74
5	n-$C_{12}H_{25}SiEt_3$ (**14**)	—	11	4
6	**14**	HCl (1.0)	100	79
7	n-$C_{12}H_{25}Si(i\text{-}Pr)_3$ (**15**)	—	9	2
8	**15**	HCl (1.0)	100	80

a) Determined by GC analysis using tetradecane as an internal standard.

Table 5. Effect of Additive in C–Si Bond Cleavage of Tetraalkylsilanes



Entry	Silane	Additive (equiv)	Conv/%[a]	Yield/%[a]
1	**14**	—	11	4
2	**14**	HCl (1.0)	100	79
3	**14**	HCl (0.1)	100	65
4	**14**	HBr (1.0)	100	93
5	**14**	H_2SO_4 (1.0)	100	75
6	**14**	NaOH (1.0)	4	1
7	**12**	—	100	72
8	**12**	NaOH (1.0)	83	58[b]
9	**12**	MeOH (1.0)	81	33[c]

a) Determined by GC analysis using tetradecane as an internal standard. b) Silanol **5** was obtained in 12%. c) Silanol **5** was obtained in 4%.

estingly, however, NaOH (1.0 equiv) did not exhibit any promoting effect (entry 6). Rather, we found that NaOH actually inhibits C–Si bond cleavage in scH_2O through control experiments using **12** as a substrate (entries 7 and 8). These results are in sharp contrast with those obtained in reactions using alkylsilanol **5** (Table 1, entries 1 and 13). We also found an inhibiting effect of MeOH (1.0 equiv) in C–Si bond cleavage (entry 9).

Conclusion

In conclusion, it was found that arylsilanes, alkenylsilanes, allylic silanes, and alkylsilanes undergo extremely facile and rapid C–Si bond cleavage in supercritical water. The rapid C–Si bond cleavage occurred even with robust unactivated tetraalkylsilanes. Control experiments revealed a dramatic difference between the supercritical and subcritical conditions, and that between supercritical water and supercritical methanol, attesting to a unique reactivity of supercritical water in C–Si bond cleavage. It is noteworthy that acids such as HCl, HBr, and H_2SO_4 promote C–Si bond cleavage in supercritical water. During this study, we also found the facile conversion of hydrosilane to silanol in supercritical water. Although further investigations are clearly needed to elucidate the mechanism of C–Si bond cleavage, the results demonstrated herein imply a unique desilylation in supercritical water, which might be useful not only in organic synthesis, but also in material manufacturing.

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz, ^{13}C 75 MHz) and JEOL A-500 (^1H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$ with chemical shifts referenced to internal standards (7.26 ppm ^1H, 77.0 ppm ^{13}C). EI and CI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. Infrared spectra were recorded on Shimadzu FTIR-8100 spectrophotometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials, anhydrous tetrahydrofuran (THF), and anhydrous diethyl ether (Et_2O) were obtained from commercial suppliers and used without further purification. Acetonitrile (CH_3CN) and triethylamine (Et_3N) were distilled over CaH_2. *N*,*N*-Dimethylformamide (DMF) was distilled over P_2O_5. Ethyl acetate (EtOAc) was distilled over K_2CO_3. *Cautionary Notes:* Although we have never experienced an accident, all reactions in supercritical water should be performed with great care due to the high temperature/pressure conditions.

Typical Procedure for the Reaction of Organosilicon Compounds in Supercritical Water (Method B, Fig. 2). Unless otherwise noted, all reactions were performed in a quartz ampoule placed in a stainless-steel tube container in order to avoid any influence of a stainless reactor (Houser's technique).[17] Quartz ampoules (inside diameter: 4.5 mm; thickness: 0.7 mm) of approximately 3 mL in total volume were used as the reactor vessels. An ampoule was filled with 0.1 mmol of organosilicon compound and 420 mg of water. After three freeze–pump–thaw cycles, the ampoule was immediately flame sealed and placed in a SUS316 stainless-steel tube (volume: 11.85 mL; lengh: 145 mm; outside diameter: 12.7 mm). The stainless tube was used as a container to hold the ampoule during heating. To avoid breakage of the quartz ampoule due to a pressure increase, a calculated amount of water was added to the stainless tube to maintain a balanced pressure. The temperature was monitored by a thermocouple inserted through the top end of the stainless-tube container. The stainless tube was submerged in a dissolved salt bath ($NaNO_2$/KNO_3), whose temperature was controlled. After a specified time, the tube was removed and cooled in an ice bath. The reaction products were analyzed by standard methods, such as capillary GC, GC–MS, and NMR. As for the silicon-containing product, we observed the formation of silica-like solid after the reactions, although it has not yet been identified.

Reactions using **3** and **4** were carried out directly in the stainless reactor (method A, Fig. 2).

Procedure for Competitive Protodesilylation of 3 and 4 in Organic Solvent (Eq. 6). To a mixture of alkenylsilane **3** (10.8 mg, 0.045 mmol), allylic silane **4** (10.8 mg, 0.045 mmol), and toluene (internal standard, 7.8 mg, 0.085 mmol) in C_6D_6 (0.6 mL) was added a drop of HI at room temperature. The resultant mixture was monitored by ^1H NMR. 1-Dodecene was formed in 0.050 mmol after standing the mixture for 15 h; 56% (0.025 mmol) of alkenylsilane **3** and 32% (0.014 mmol) of allylic silane **4** remained unchanged. The isomerization of 1-dodecene to other dodecenes was not observed under these conditions.

(4-Butylphenyl)trimethylsilane (2). To a solution of 1,4-dibromobenzene (12.76 g, 50.0 mmol) in Et_2O (100 mL) was added a solution of BuLi (50.0 mmol, 1.53 M) in hexane at −78 °C and the reaction mixture was stirred at −78 °C for 4 h. To this mixture was added chlorotrimethylsilane (6.18 g, 56.8 mmol) at −78 °C and the reaction mixture was stirred for 10 min. After the mixture was stirred at room temperature for 2 h, H_2O was added to the mixture, and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was washed with brine. Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded (4-bromophenyl)-trimethylsilane quantitatively.

To a solution of (4-bromophenyl)trimethylsilane (5.63 g, 24.7 mmol) in THF (50 mL) was added a solution of BuLi (29.6 mmol, 1.53 M) in hexane at room temperature. After the mixture was stirred at room temperature for 2 h, H_2O was added to the mixture, and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded **2** (3.04 g, 60%) as a colorless liquid: bp 136 °C/27 mmHg. ^1H NMR (300 MHz) δ 0.25 (s, 9H), 0.93 (t, $J = 7.5$ Hz, 3H), 1.30–1.45 (m, 2H), 1.55–1.65 (m, 2H), 2.60 (t, $J = 7.5$ Hz, 2H), 7.19 (d, $J = 7.8$ Hz, 2H), 7.44 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (75 MHz) δ −1.1, 14.0, 22.4, 33.6, 35.6, 127.9, 133.3, 137.0, 143.6. HRMS (EI) m/z calcd for $C_{13}H_{22}Si$: 206.1491, found 206.1493. Anal. Calcd for $C_{13}H_{22}Si$: C, 75.65; H, 10.74%. Found: C, 75.95; H, 10.84%.

(*E*)-1-Dodecenyltrimethylsilane (3). Compound **3** was prepared using a procedure developed by Chan.[47] To a suspension of $KOBu^t$ (8.41 g, 74.9 mmol) in hexane (40 mL) was added a solution of BuLi (75.0 mmol, 1.57 M) in hexane at 0 °C, and the mixture was stirred at 0 °C for 10 min and at room temperature for 35 min. To this mixture were added Et_2O (50 mL) and allyltrimethylsilane (8.70 g, 76.1 mmol) at −78 °C. After the mixture was stirred at 0 °C for 1 h, a solution of 1-bromononane (15.63 g, 75.4 mmol) in Et_2O (20 mL) was added to the mixture at −78 °C. After the mixture was stirred at room temperature for 14 h, H_2O was added to the mixture and the organic phase was separated. The organic phase was washed with aq $Na_2S_2O_3$ solution. Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **3** (8.69 g, 48%) as a colorless liquid: ^1H NMR (300 MHz) δ 0.04 (s, 9H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.45 (m, 16H), 2.09 (td, $J = 6.9$, 6.3 Hz, 2H), 5.61 (dt, $J = 18.3$, 1.5 Hz, 1H), 6.02 (dt, $J = 18.3$, 6.3 Hz, 1H). ^{13}C NMR (125 MHz) δ −1.1, 14.1, 22.7, 28.7, 29.2, 29.4, 29.5, 29.63, 29.64, 31.9, 36.8, 129.4, 147.4. HRMS (EI) m/z calcd for $C_{15}H_{32}Si$: 240.2273, found 240.2274. Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41%. Found: C, 74.61; H, 13.70%.

2-Dodecenyltrimethylsilane (4). Compound **4** was prepared using a procedure developed by Tsuji.[48] To a solution of vinylmagnesium bromide (60.0 mmol, 1.0 M) in THF was added decanal (7.86 g, 50.3 mmol) at 0 °C. After the mixture was stirred at 0 °C for 1 h and then at room temperature for 66 h, an aq HCl solution was added to the mixture, and the organic phase was separated. The aqueous phase was extracted with Et_2O (four times). The combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded dodec-1-en-3-ol (7.92 g, 86%) as a colorless liquid: bp 82 °C/1.2 mmHg. ^1H NMR (300 MHz) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.15–1.40 (m, 14H), 1.45–1.60 (m, 3H), 4.09 (qt, $J = 6.6$, 1.2 Hz, 1H), 5.10 (dt, $J = 10.5$, 1.5 Hz, 1H), 5.22 (dt, $J = 17.1$, 1.5 Hz, 1H), 5.87 (ddd, $J = 17.1$, 10.5, 6.6 Hz, 1H).

To a solution of dodec-1-en-3-ol (9.22 g, 50.0 mmol), triethylamine (6.07 g, 60.0 mmol), and 4-(dimethylamino)pyridine (619 mg, 5.07 mmol) in CH_2Cl_2 (50 mL) was added trifluoroacetic anhydride (13.01 g, 61.9 mmol) at 0 °C. After the mixture was stirred at 0 °C for 2 h, and then at room temperature for 2 h, H_2O was added to the mixture, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (four times). The combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded 3-trifluoroacetoxy-1-dodecene (11.40 g, 81%) as a colorless liquid: bp 69 °C/1.1 mmHg. ^1H NMR (300 MHz) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.15–1.40 (m, 14H), 1.60–1.85 (m, 2H), 5.29 (d, $J = 10.5$ Hz, 1H), 5.35 (d, $J = 17.4$ Hz, 1H), 5.37 (q, $J = 6.9$ Hz, 1H), 5.80 (ddd, $J = 17.4$, 10.5, 6.9 Hz, 1H).

A solution of [$Pd(dba)_2$] (345 mg, 0.60 mmol, 3 mol%), hexamethyldisilane (5.85 g, 40.0 mmol), and 3-trifluoroacetoxy-1-dodecene (5.63 g, 20.1 mmol) in THF (110 mL) was stirred at room temperature for 6 h. The removal of the solvents under reduced pressure and subsequent distillation afforded **4** (4.20 g, 87%, $E/Z = 92/8$) as colorless liquid: bp 85–86 °C/0.8 mmHg. ^1H NMR (300 MHz) δ −0.02 (s, 9H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.35 (m, 14H), 1.39 (d, $J = 7.5$ Hz, 2H), 1.96 (q, $J = 6.9$ Hz, 2H), 5.23 (dt, $J = 15.1$, 6.9 Hz, 1H), 5.36 (dt, $J = 15.1$, 7.5 Hz, 1H). ^{13}C NMR (75 MHz) δ −2.0, 14.1, 22.6, 22.7, 29.1, 29.4, 29.5, 29.6, 30.0, 31.9, 32.8, 125.9, 129.0. HRMS (EI) m/z calcd for $C_{15}H_{32}Si$: 240.2273, found 240.2273.

1-Dodecyldimethylsilanol (5). Compound **5** was prepared using a procedure developed by Chang.[49] The mixture of **11** (6.23 g, 27.3 mmol), [$RuCl_2(p\text{-cymene})]_2$ (334 mg, 0.55 mmol, 2 mol%), and H_2O (970 mg, 54.5 mmol) in CH_3CN (82 mL) was stirred at room temperature for 4 h under air. Removal of the solvents under reduced pressure and subsequent distillation afforded **5** (3.97 g, 60%) as a colorless liquid: bp 109 °C/0.8 mmHg. ^1H NMR (300 MHz) δ 0.12 (s, 6H), 0.55–0.63 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.40 (m, 21H). ^{13}C NMR (125 MHz) δ −0.3, 14.1, 17.8, 22.7, 23.1, 29.36, 29.38, 29.58, 29.65, 29.68, 29.7, 31.9, 33.4. HRMS (CI) m/z calcd for $C_{14}H_{33}OSi$ [M + H]: 245.2301, found 245.2293.

2-Dodecyldimethylsilanol (6). To a suspension of Mg (244.3 mg, 10.0 mmol) in Et_2O (4 mL) was added a solution of 2-bromododecane (2.51 g, 10.1 mmol) in Et_2O (2 mL) at room temperature. The reaction mixture was stirred for 2 h, and chlorodimethylsilane (1.27 g, 13.5 mmol) was added to the mixture at room temperature. After stirring the mixture at room temperature for 14 h, H_2O was added to the mixture, and the organic phase was separated. The organic phase was washed with brine. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded 2-dodecyldimethylsilane (1.52 g, 66%) as colorless liquid: bp 96 °C/1.5 mmHg. ^1H NMR (300 MHz) δ 0.03 (d, $J = 3.6$ Hz, 3H), 0.04 (d, $J = 3.6$ Hz, 3H), 0.65–0.80 (m, 1H), 0.88 (t, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 7.2$ Hz, 3H), 1.15–1.35 (br, 16H), 1.35–1.50 (m, 2H), 3.70–3.80 (m, 1H).

A mixture of 2-dodecyldimethylsilane (728.2 mg, 3.19 mmol), [$RuCl_2(p\text{-cymene})]_2$ (36.7 mg, 0.06 mmol, 2 mol%), and H_2O (114.4 mg, 6.35 mmol) in CH_3CN (10 mL) was stirred at room temperature for 5 h under air. Removal of the solvents under reduced pressure and subsequent silica-gel chromatography afforded **6** (642.4 mg, 82%) as colorless oil. ^1H NMR (300 MHz) δ 0.10 (s, 6H), 0.60–0.75 (m, 1H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 7.2$ Hz, 3H), 1.20–1.35 (m, 16H), 1.40–1.50 (m, 3H). ^{13}C NMR (125

MHz) δ −2.1, −2.0, 13.4, 14.1, 20.9, 22.7, 28.6, 29.3, 29.6 (two carbons), 29.7, 29.8, 31.1, 31.9. HRMS (EI) m/z calcd for $C_{14}H_{32}OSi$: 244.2222, found 244.2223.

Chloro(1-dodecyl)dimethylsilane (7). To a solution of dichlorodimethylsilane (21.4 g, 165.8 mmol) in THF (40 mL) was added a solution of 1-dodecylmagnesium bromide (78 mmol, 1.56 M) in THF at room temperature. After stirring the mixture at room temperature for 16 h, hexane (60 mL) was added to the mixture. Filtration through Celite®, removal of the solvents under reduced pressure, and distillation afforded **7** (17.6 g, 86%) as a colorless liquid: bp 105 °C/0.25 mmHg. ^{1}H NMR (300 MHz) δ 0.40 (s, 6H), 0.75–0.85 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.45 (m, 20H). ^{13}C NMR (125 MHz) δ 1.7, 14.1, 19.0, 22.7, 23.0, 29.3, 29.4, 29.5, 29.66, 29.68, 29.69, 31.9, 33.0. HRMS (EI) m/z calcd for $C_{14}H_{31}ClSi$: 262.1884, found 262.1885.

1-Dodecyl(ethoxy)dimethylsilane (8). To a solution of imidazole (1.71 g, 25.2 mmol) and ethanol (1.18 g, 25.6 mmol) in DMF (45 mL) was added **7** (6.67 g, 25.4 mmol) at 0 °C. After stirring the mixture at room temperature for 19 h, brine was added to the mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times), and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded **8** (3.97 g, 57%) as colorless liquid: bp 102 °C/1.1 mmHg. ^{1}H NMR (300 MHz) δ 0.08 (s, 6H), 0.50–0.62 (m, 2H), 0.87 (t, $J = 6.6$ Hz, 3H), 1.18 (t, $J = 7.2$ Hz, 3H), 1.20–1.40 (m, 20H), 3.65 (q, $J = 7.2$ Hz, 2H). ^{13}C NMR (125 MHz) δ −2.1, 14.1, 16.4, 18.5, 22.7, 23.2, 29.4 (two carbons), 29.59, 29.66, 29.69, 29.71, 31.9, 33.5, 58.2. IR (neat) 2957, 2924, 2855, 1466, 1458, 1250, 1109, 1082, 947, 839, 779 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{37}OSi$ [M + H]: 273.2614, found 273.2614.

1,3-Di(1-dodecyl)-1,1,3,3-tetramethyldisiloxane (9). To a solution of **5** (717 mg, 2.93 mmol) and triethylamine (296 mg, 2.93 mmol) in EtOAc (3 mL) was added **7** (828 mg, 2.93 mmol) at room temperature. After stirring the mixture at room temperature for 22 h, H_2O was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et_2O (five times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent silica-gel chromatography (hexane) afforded **9** (1.13 g, 82%) as colorless oil: ^{1}H NMR (300 MHz) δ 0.02 (s, 12H), 0.45–0.55 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 6H), 1.20–1.35 (m, 40H). ^{13}C NMR (125 MHz) δ 0.4, 14.1, 18.4, 22.7, 23.3, 29.40, 29.45, 29.65, 29.70, 29.74, 29.76, 32.0, 33.5. HRMS (CI) m/z calcd for $C_{28}H_{63}OSi_2$ [M + H]: 471.4417, found 471.4423.

1-(1-Dodecyl)-1,1,2,2,2-pentamethyldisilane (10). To a suspension of Mg (609 mg, 25.1 mmol) in Et_2O (7 mL) was added a solution of 1-bromododecane (6.31 g, 25.3 mmol) in Et_2O (6 mL) at 0 °C and the mixture was stirred at room temperature for 4 h. Chloropentamethyldisilane (4.19 g, 25.1 mmol) was then added to the reaction mixture at room temperature. After stirring the mixture at room temperature for 12 h, an aq HCl solution was added to the reaction mixture, and the organic phase was separated. The aqueous phase was extracted with Et_2O (five times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded **10** (4.10 g, 54%) as colorless liquid: bp 121 °C/1.1 mmHg. ^{1}H NMR (300 MHz) δ 0.01 (s, 6H), 0.04 (s, 9H), 0.50–0.60 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H), 1.20–1.35 (m, 20H). ^{13}C NMR (125 MHz) δ −4.3, −2.0, 14.1, 14.9, 22.7, 24.6, 29.4 (two carbons), 29.64, 29.68, 29.71, 29.73, 31.9, 33.8. HRMS (EI) m/z calcd for $C_{17}H_{40}Si_2$: 300.2669, found 300.2666.

1-Dodecyldimethylsilane (11). To a suspension of Li (596 mg, 85.2 mmol) in Et_2O (20 mL) was added a solution of 1-bromododecane (10.63 g, 42.6 mmol) in Et_2O (30 mL) at 0 °C. The reaction mixture was stirred for 4 h, and chlorodimethylsilane (4.34 g, 45.9 mmol) was added to the mixture at 0 °C. After stirring the mixture at room temperature for 14 h, H_2O was added to the mixture and the organic phase was separated. The organic phase was washed with brine. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded **11** (6.24 g, 64%) as a colorless liquid: bp 84 °C/0.8 mmHg. ^{1}H NMR (300 MHz) δ 0.05 (d, $J = 3.6$ Hz, 6H), 0.50–0.62 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.40 (m, 20H), 3.83 (heptet, $J = 3.6$ Hz, 1H). ^{13}C NMR (125 MHz) δ −4.4, 14.1, 14.2, 22.7, 24.4, 29.38, 29.40, 29.60, 29.67, 29.70, 29.72, 31.9, 33.3. HRMS (EI) m/z calcd for $C_{14}H_{31}Si$ [M − H]: 227.2195, found 227.2200.

1-Dodecyltrimethylsilane (12). To a suspension of Li (418 mg, 60.2 mmol) in Et_2O (10 mL) was added a solution of 1-bromododecane (7.63 g, 30.6 mmol) in Et_2O (10 mL) at 0 °C, and the mixture was stirred at 0 °C for 2 h. Chlorotrimethylsilane (3.80 g, 35.0 mmol) was then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 10 h, H_2O was added to the reaction mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over Na_2SO_4. Removal of the solvents under reduced pressure and subsequent distillation afforded **12** (2.28 g, 31%) as a colorless liquid: bp 86 °C/1.0 mmHg. ^{1}H NMR (300 MHz) δ −0.04 (s, 9H), 0.42–0.50 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.35 (m, 20H). ^{13}C NMR (75 MHz) δ −1.6, 14.1, 16.7, 22.7, 23.9, 29.39, 29.43, 29.64, 29.67, 29.70, 29.74, 31.9, 33.7. HRMS (EI) m/z calcd for $C_{14}H_{31}Si$ [M − Me]: 227.2195, found 227.2197. Anal. Calcd for $C_{15}H_{34}Si$: C, 74.29; H, 14.13%. Found: C, 74.45; H, 14.26%.

2-Dodecyltrimethylsilane (13). To a suspension of Mg (246 mg, 10.1 mmol) in THF (3 mL) were added a few drops of 1,2-dibromoethane, and then a solution of 2-bromododecane (2.49 g, 10.0 mmol) in THF (3 mL) at room temperature and the mixture was stirred at room temperature for 1 h. Chlorotrimethylsilane (1.20 g, 11.0 mmol) and CuCN[50] (50.2 mg, 0.55 mmol) were then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 16 h, an aq NaOH solution was added to the reaction mixture at 0 °C and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent gel permeation chromatography afforded **13** (534 mg, 22%) as a colorless liquid: ^{1}H NMR (500 MHz) δ −0.07 (s, 9H), 0.51–0.58 (m, 1H), 0.87 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 7.3$ Hz, 3H), 1.00–1.30 (m, 18H). ^{13}C NMR (125 MHz) δ −3.2, 14.0, 14.1, 19.5, 22.7, 28.6, 29.4, 29.67, 29.71, 29.75, 29.83, 31.7, 31.9. IR (neat) 2955, 2855, 1489, 1466, 1248, 855, 833, 749, 689 cm^{-1}. HRMS (EI) m/z calcd for $C_{15}H_{34}Si$: 242.2430, found 242.2435. Anal. Calcd for $C_{15}H_{34}Si$: C, 74.29; H, 14.13%. Found: C, 74.18; H, 13.90%.

1-Dodecyltriethylsilane (14). To a suspension of Li (406 mg, 58.5 mmol) in Et_2O (10 mL) was added a solution of 1-bromododecane (7.25 g, 29.1 mmol) in Et_2O (10 mL) at 0 °C, and the mixture was stirred at 0 °C for 2 h. Chlorotriethylsilane (4.87 g, 32.3 mmol) was then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 16 h, H_2O was added to the reaction mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure and subsequent distillation afforded **14** (5.08 g, 61%) as a colorless liquid: bp 114 °C/1.0 mmHg. ^1H NMR (300 MHz) δ 0.45–0.48 (m, 2H), 0.49 (q, $J = 7.8$ Hz, 6H), 0.88 (t, $J = 6.9$ Hz, 3H), 0.92 (t, $J = 7.8$ Hz, 9H), 1.20–1.30 (m, 20H). ^{13}C NMR (125 MHz) δ 3.4, 7.5, 11.3, 14.1, 22.7, 23.9, 29.4 (two carbons), 29.66, 29.69, 29.73, 29.76, 32.0, 34.0. HRMS (EI) m/z calcd for $C_{16}H_{35}Si$ [M − Et]: 255.2508, found 255.2504.

1-Dodecyltriisopropylsilane (15). To a suspension of Li (283 mg, 40.8 mmol) in Et_2O (8 mL) was added a solution of 1-bromododecane (5.08 g, 20.4 mmol) in Et_2O (8 mL) at 0 °C, and the mixture was stirred at 0 °C for 3 h. To this mixture were added triisopropylsilyl triflate (6.87 g, 22.4 mmol) and then hexamethylphosphoramide (8 mL) at 0 °C. After stirring the mixture at 0 °C for 2 h, and then at room temperature for 15 h, H_2O was added to the reaction mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Filtration through a short silica gel pad (hexane), removal of the solvents under reduced pressure, and subsequent distillation afforded **15** (1.51 g, 23%) as a colorless liquid: bp 132 °C/0.9 mmHg. ^1H NMR (300 MHz) δ 0.50–0.60 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 0.95–1.00 (m, 3H), 1.02 (s, 18H), 1.20–1.40 (m, 20H). ^{13}C NMR (125 MHz) δ 9.4, 11.0, 14.1, 18.9, 22.7, 24.3, 29.3, 29.4, 29.68 (two carbons), 29.73, 29.74, 32.0, 34.5. IR (neat) 2959, 2924, 1464, 884, 733, 693, 656 cm^{-1}. HRMS (EI) m/z calcd for $C_{18}H_{39}Si$ [M − ^{i}Pr]: 283.2821, found 283.2813. Anal. Calcd for $C_{21}H_{46}Si$: C, 77.21; H, 14.19%. Found: C, 77.04; H, 14.45%.

Tetra(1-dodecyl)silane (16). To a suspension of Li (304 mg, 43.8 mmol) in Et_2O (10 mL) was added a solution of 1-bromododecane (5.51 g, 22.1 mmol) in Et_2O (10 mL) at 0 °C, and the mixture was stirred at 0 °C for 5 h. To this mixture was added tetrachlorosilane (538 mg, 3.17 mmol) at 0 °C. After stirring the mixture at 0 °C for 1 h and then at room temperature for 70 h, H_2O was added to the reaction mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (three times) and the combined organic phase was dried over $MgSO_4$. Removal of the solvents under reduced pressure, and subsequent gel permeation chromatography afforded **16** (1.81 g, 81%) as colorless oil. ^1H NMR (300 MHz) δ 0.40–0.50 (m, 8H), 0.88 (t, $J = 7.2$ Hz, 12H), 1.20–1.35 (br, 80H). ^{13}C NMR (125 MHz) δ 12.5, 14.1, 22.7, 23.9, 29.34, 29.40, 29.66, 29.70, 29.74, 29.76, 32.0, 33.9. IR (neat) 2922, 2853, 1466, 766, 722 cm^{-1}. HRMS (EI) m/z calcd for $C_{36}H_{75}Si$ [M − $C_{12}H_{25}$]: 535.5638, found 535.5637.

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