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Efficient and Rapid C−Si Bond Cleavage in Supercritical Water

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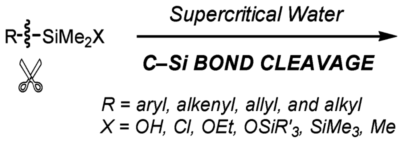
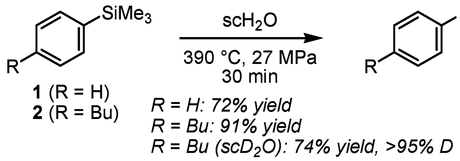
Supercritical water (scH_2O), the critical temperature and pressure of which are 374 °C and 22.1 MPa, respectively, has been attracting increasing attention because of its unique physical and chemical properties that are very different from those of ambient water.[1] For example, because the dielectric 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 the constant-pressure condition. Although scH_2O has tended to be used as a medium for the degradation of toxic materials, waste synthetic polymers, and biomass, chemists have recently set out to use scH_2O as a medium for chemical synthesis.[2]

Organosilicon compounds have been extensively utilized in modern organic synthesis.[3] However, their use in scH_2O has not been reported to date. 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. We report herein an extremely facile C−Si bond cleavage of organosilicon compounds in scH_2O (eq 1), which serves as a starting point toward the development of silicon-based organic synthesis in scH_2O.



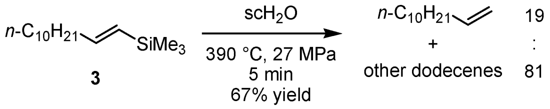
(1)

Electrophilic cleavage of arylsilanes has been extensively utilized in organic synthesis because a coming electrophile always occupies the position where the silyl group has been attached (*ipso* substitution).[4] Thus, we began our research by subjecting arylsilanes to scH_2O (eq 2).[5] When **1** and **2** were employed, protodesilylation occurred within 30 min at 390 °C to give benzene derivatives in high yields. 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.[4]



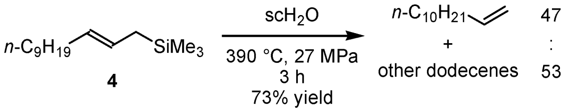
(2)

Encouraged by these promising results, we undertook the investigation of C−Si bond cleavage of the other class of nucleophilic organosilicon compounds, alkenylsilanes and allylic silanes, in scH_2O.[6] When alkenylsilane **3** was subjected into scH_2O (390 °C, 5 min), a mixture of dodecenes was obtained in 67% yield (eq 3). The initial desilylation product (1-dodecene) seemed to isomerize into thermodynamically more stable inner alkenes under the reaction conditions.[7] Indeed, the ratio of 1-dodecene/other dodecenes increased (84/16) as the reaction time was shortened to 1 min.



(3)

Similarly, allylic silane **4** also underwent rapid desilylation in scH_2O (eq 4). However, it was surprising to observe that 47% of 1-dodecene remained even after a prolonged reaction time (3 h). Shortening the reaction time resulted in the recovery of starting allylic silane **4**. Quite interestingly, the competitive reaction of **3** and **4** indicated the faster desilylation of **3** in scH_2O, although the opposite reactivity order is generally observed in the reaction with electrophiles.[8] In fact, we found that **4** was more reactive than **3** under typical desilylation conditions (HI in C_6D_6 at room temperature).[9] Therefore, the preliminary results demonstrated herein imply a unique desilylation in scH_2O.



(4)

We next examined the reaction of alkylsilanes, which are known to be much less reactive toward C−Si bond cleavage than the organosilanes mentioned before (Table 1).[3] We found that the C−Si bond cleavage of alkylsilanes having a heteroatom on silicon took place efficiently.[10] For example, silanol **5** underwent efficient C−Si bond cleavage at 390 °C, giving dodecane in 68% yield (run 1). Raising the temperature had little effect on the product yield (run 2). However, the desilylation was extremely sluggish at 350 °C (subcritical conditions), and the corresponding siloxane **8** was formed in 30% yield (run 3). Interestingly, it was found that the addition of either HCl or NaOH had a beneficial effect on the C−Si bond cleavage (runs 4 and 5). When **5** was subjected into supercritical methanol, no C−Si bond cleavage occurred, and only the corresponding methoxysilane was detected (run 6). The reaction using chlorosilane **6** gave dodecane in 89% yield (run 7). The higher yield as compared to that with **5** may be due to the effect of HCl generated in situ. Although the desilylation was less efficient when ethoxysilane **7**, siloxane **8**, and disilane **9** were used (runs 8, 10, and 12), the addition of HCl gave rise to higher yields of the desilylation products (runs 9, 11, and 13).

The successful desilylation of functionalized alkylsilanes finally led us to the ultimate challenge, the C−Si bond cleavage of unactivated tetraalkylsilanes.[11] Beyond our imagination, this trans-

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Table 1. C−Si Bond Cleavage of Functionalized Alkylsilanes in scH$_2$O

$$n\text{-}C_{12}H_{25}{-}SiMe_2X \xrightarrow[\text{temp, 3 h}\ \text{additive}]{scH_2O} n\text{-}C_{12}H_{25}{-}H$$

run	X	temp (°C)	additive[a]	yield (%)[b]
1	OH (**5**)	390		68
2	OH (**5**)	410		66
3	OH (**5**)	350		11[c]
4	OH (**5**)	390	HCl	88
5	OH (**5**)	390	NaOH	85
6	OH (**5**)	390		0[d]
7	Cl (**6**)	390		89
8	OEt (**7**)	390		23
9	OEt (**7**)	390	HCl	72
10	$OSiMe_2C_{12}H_{25}$ (**8**)	390		46
11	$OSiMe_2C_{12}H_{25}$ (**8**)	390	HCl	88
12	$SiMe_3$ (**9**)	390		56
13	$SiMe_3$ (**9**)	390	HCl	91

[a] 1.0 equivalent to alkylsilanes. [b] Determined by GC analysis using tetradecane as an internal standard. [c] Siloxane **8** was formed in 30% yield. [d] Reaction was performed in supercritical methanol. $C_{12}H_{25}SiMe_2OMe$ was formed in 53% yield.

Table 2. C−Si Bond Cleavage of Tetraalkylsilanes in scH$_2$O

$$C_{12}H_{25}{-}SiR_3 \longrightarrow C_{12}H_{25}{-}H$$

n-$C_{12}H_{25}$-$SiMe_3$ (**10**), *n*-$C_{10}H_{21}CH(CH_3)$-$SiMe_3$ (**11**),
n-$C_{12}H_{25}$-$SiEt_3$ (**12**), *n*-$C_{12}H_{25}$-Si(*i*-Pr)$_3$ (**13**), (*n*-$C_{12}H_{25}$)$_4$Si (**14**)

run	silane	media	temp (°C)	time (h)	additive[a]	yield (%)[b]
1	**10**	H_2O	390	0.5		72 (100)
2	**10**	H_2O	390	0.5	HCl	88 (100)
3	**10**	H_2O	350	0.5		11 (35)[c]
4	**10**	H_2O	110	14	HCl	0 (4)
5	**10**	MeOH	390	0.5		1 (20)
6	**11**	H_2O	390	0.5		0.4 (8)
7	**11**	H_2O	390	0.5	HCl	74 (100)
8	**12**	H_2O	390	0.5		4 (11)
9	**12**	H_2O	390	0.5	HCl	79 (100)
10	**13**	H_2O	390	0.5		2 (9)
11	**13**	H_2O	390	0.5	HCl	80 (100)
12	**14**	H_2O	390	0.5	HCl	368

[a] 1.0 equivalent to alkylsilanes. [b] Determined by GC analysis using tetradecane as an internal standard. The figure in parentheses is the conversion (%) of tetraalkylsilane. [c] Silanol **5** (9%) was detected.

formation was found to be extremely rapid in scH$_2$O (Table 2). Primary alkyltrimethylsilane **10** underwent expeditious C−Si bond cleavage at 390 °C within 30 min, giving dodecane in 72% yield (run 1).[12] By adding HCl, we increased the yield to 88% (run 2). The desilylation was extremely inefficient in subcritical water (run 3) or entirely sluggish in refluxing HCl/H_2O (run 4) or in supercritical methanol (run 5). The desilylation of secondary alkylsilane **11** was less efficient (0.4%) at 390 °C (run 6). 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 (runs 8 and 10). Such a considerable reactivity difference may be useful for the 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 within 30 min (runs 7, 9, and 11). When **14** was used as a substrate, 368% of 1-dodecane was formed (run 12). This result unambiguously verifies that all C−Si bonds of tetraalkylsilanes are cleaved in scH$_2$O.

The realization of C−Si bond cleavage of robust unactivated tetraalkylsilane in scH$_2$O is interesting because it does not require strong Lewis acids such as $AlCl_3$ as promoters.[11] Moreover, the control experiments revealed the dramatic difference between supercritical and subcritical conditions (run 1 vs run 3) and that between scH$_2$O and scMeOH (run 1 vs run 5), attesting to a unique reactivity of scH$_2$O in C−Si bond cleavage.

In summary, aryl-, alkenyl-, allyl-, and alkylsilanes were found to undergo extremely facile C−Si bond cleavage in scH$_2$O. Particularly, the finding that robust tetraalkylsilanes could also undergo rapid C−Si bond cleavage is extremely intriguing and would help to alter the chemist's impression that the trialkylsilyl group may be a dead-end for manipulating alkylsilanes.[11] With this desilylation in hand, the trialkylsilyl group can now be regarded as a removable group that is expected to exert steric and electronic controls over numerous reactions. The effort to develop silicon-based organic synthesis in scH$_2$O is now in progress.

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Supporting Information Available: Experimental procedures and analytical and spectroscopic data of compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) To exclude any positive or negative effect of the stainless steel reactor, most of the reactions in this study were performed in a sealed quartz tube placed in a stainless steel reactor (SUS316).

(6) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(7) When 1-dodecene was subjected in scH$_2$O (390 °C), complete isomerization into inner alkenes was observed within 3 h.

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(11) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, Chapter 9.1. Armitage has noted in this comprehensive review: "Tetraalkylsilanes are remarkably stable compounds. The silicon−carbon bond is strong and almost nonpolar. It is therefore only broken under the most vigorous conditions, unless assisted by an alkyl group possessing an activating substituent suitably placed." Representative methods of C−Si bond cleavage of tetraalkylsilane are collected in this review. For relatively recent examples on this subject, see: Kakiuchi, F.; Furuta, K.; Murai, S.; Kawasaki, Y. *Organometallics* **1993**, *12*, 15. Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1996**, *61*, 6044.

(12) When the reaction was performed directly in a stainless reactor, desilylation was quite inefficient (57% conversion; dodecane 19%; **5** 29%). Therefore, in this particular class of compounds (tetraalkylsilanes), the inhibiting effect of the stainless steel reactor (SUS316) and/or the promoting effect of the quartz tube might be involved for C−Si bond cleavage.

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