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Chemoselective Cleavage of Si−C(sp^3) Bonds in Unactivated Tetraalkylsilanes Using Iodine Tris(trifluoroacetate)

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ABSTRACT: Organosilanes are synthetically useful reagents and precursors in organic chemistry. However, the typical inertness of unactivated Si−C(sp^3) bonds under conventional reaction conditions has hampered the application of simple tetraalkylsilanes in organic synthesis. Herein we report the chemoselective cleavage of Si−C(sp^3) bonds of unactivated tetraalkylsilanes using iodine tris(trifluoroacetate). The reaction proceeds smoothly under mild conditions (−50 °C to room temperature) and tolerates various polar functional groups, thus enabling subsequent Tamao−Fleming oxidation to provide the corresponding alcohols. NMR experiments and density functional theory calculations on the reaction indicate that the transfer of alkyl groups from Si to the I(III) center and the formation of the Si−O bond proceed concertedly to afford an alkyl-λ^3-iodane and silyl trifluoroacetate. The developed method enables the use of unactivated tetraalkylsilanes as highly stable synthetic precursors.

Silyl groups are stable and easy-to-handle synthetic linchpins that can be converted into various functional groups via oxidation, halogenation, and cross-coupling reactions.[1] While transformations of arylsilane derivatives have been widely studied, alkylsilanes have attracted less attention in organic synthesis because of their lower reactivity. A notable exception is the Tamao−Fleming oxidation,[2] which transforms alkylsilanes into the corresponding alcohols, typically using peroxides and fluoride activators. These protocols have often been employed in the total synthesis of complex natural products.[3] Nevertheless, to facilitate oxidation of the silyl groups, the silicon atom must carry at least one heteroatomic functional group or aryl/allyl substituent, which can be selectively converted into a heteroatomic functional group through electrophilic transformations.[4] Simple, unactivated tetraalkylsilanes are unreactive under conventional organic synthesis reaction conditions, including those of the Tamao−Fleming oxidation. The synthetic utility of trialkylsilyl groups (e.g., $-SiMe_3$ and $-SiEt_3$) in aliphatic backbones has scarcely been explored.[5] However, the high stability of tetraalkylsilanes and the low cost of some trialkylsilyl reagents would make the application of tetraalkylsilanes as synthetic precursors attractive if the Si−C(sp^3) bond could be cleaved under mild reaction conditions.

Cleavage of the Si−C(sp^3) bonds in unactivated tetraalkylsilanes has to date mainly been accomplished by protodesilylation reactions using strong Brønsted acids,[6] redistribution reactions using strong Lewis acids,[7] or oxidation reactions using highly electrophilic reagents.[8] In most of those previous studies, the substrates have been limited to Me_4Si or other tetraalkylsilanes that do not carry polar functional groups, and the functional group tolerance has not yet been investigated (Scheme 1a). In 1993, Murai and coworkers reported the oxidative cleavage of unactivated Si−C(sp^3) bonds in a hydroxy-group-containing tetraalkylsilane using a phenylthallium(III) complex (Scheme 1b).[9] More recently, Suginome and co-workers developed a stepwise approach to convert trimethylsilyl groups into hydroxy groups via Ir-catalyzed C−H borylation of a Me group and three subsequent oxidative transformations in the presence of ester or ether functionalities (Scheme 1c).[10a] However, only very few oxygen-containing substrates were examined in those reports. Thus, the development of general methods for the cleavage of unactivated Si−C(sp^3) bonds that can tolerate various polar functional groups is important for the further expansion of the application of tetraalkylsilanes in organic chemistry.[10b]

Herein we report the chemoselective cleavage of Si−C(sp^3) bonds in unactivated tetraalkylsilanes containing a wide range of polar functional groups using iodine tris(trifluoroacetate) (ITT) (Scheme 1d). We discovered that ITT reacts with various tetraalkylsilanes under mild reaction conditions (−50 °C to room temperature) to cleave Si−C(sp^3) bonds. The resulting intermediates can be further converted into the corresponding alcohols via subsequent oxidation with H_2O_2.

During our studies on the reactivity of ITT and $I(OAc)_3$ in organic synthesis,[11,12] we envisioned that the high electrophilicity of ITT could potentially enable the cleavage of unreactive electron-rich covalent bonds, including Si−C(sp^3) bonds. We initially attempted the reaction of ITT with Me_4Si (**A**) in $CDCl_3$ at room temperature (Scheme 2). To our delight, the cleavage of one Si−C(sp^3) bond of **A** proceeded

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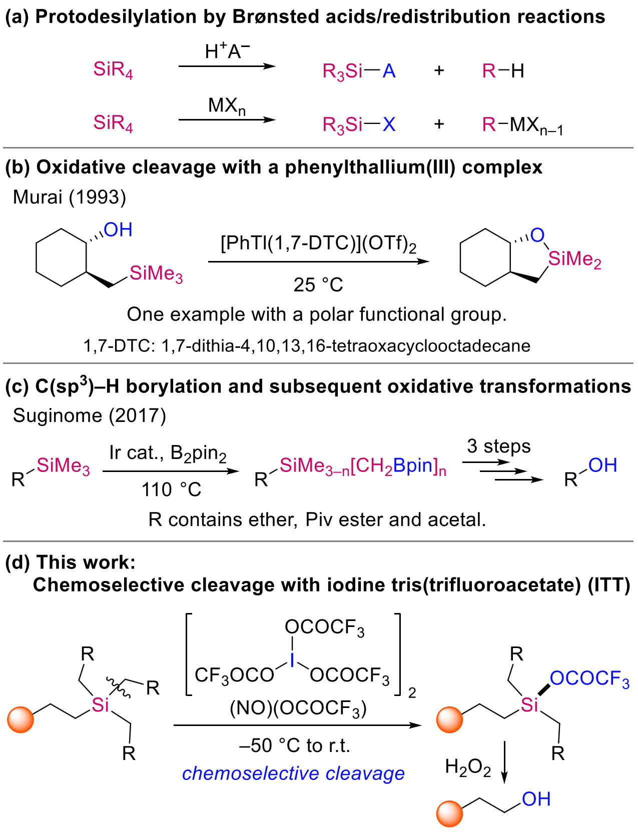
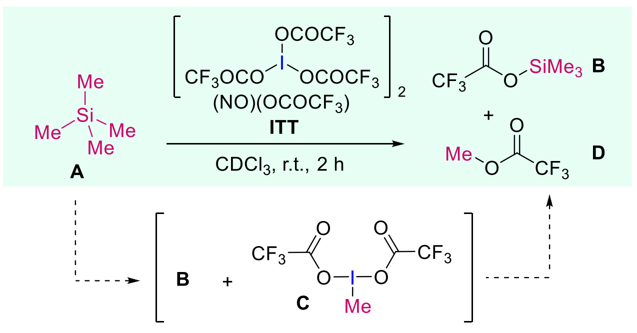
Scheme 1. Cleavage of Si–C(sp^3) Bonds of Unactivated Tetraalkylsilanes



Scheme 2. Reaction of Me_4Si (A) with ITT as Determined Using NMR Analysis



smoothly to afford trimethylsilyl trifluoroacetate ($Me_3SiOTFA$, **B**) and methyl trifluoroacetate (MeOTFA, **D**), as confirmed via ^1H and ^{19}F NMR analysis (for details, see Figures S1 and S2). On the basis of this result and the fact that the I(III) center of ITT is highly electrophilic,[11,12] we speculated that the reaction would initially afford methyl-λ^3-iodane **C** via electrophilic Me transfer to form the I(III)–Me bond. Subsequently, **C** could be decomposed into **D**.[13]

To support this hypothesis, we carried out density functional theory (DFT) calculations of the reaction of **A** with ITT at the M06-2X/def2-TZVPPD+SMD(CH_2Cl_2)//M06-2X/def2-SVP level of theory. While a dimeric crystal structure has been reported for ITT,[12d] our DFT calculations suggested that the monomeric structure **ITT_I** is more stable in solution. After intensive investigations, the transition-state structure and reaction pathway leading to electrophilic Si–Me cleavage were identified (Figure 1). The reaction pathway involves the slightly unstable conformational isomer **ITT_II**. The electrophilic transfer of Me from **A** to the I(III) center of **ITT_II** and the formation of the Si–O bond proceed in a concerted fashion. In this transition state, the I(III) center attacks the Me group from the side opposite the silicon atom. Similar electrophilic methyl inversion has been reported by Qu and Oestreich in their protodesilylation reaction.[6f,g] The calculated activation energy is qualitatively reasonable (22.1 kcal mol^{-1}), and the formation of **B** and **C** is highly exergonic (−61.4 kcal mol^{-1}).

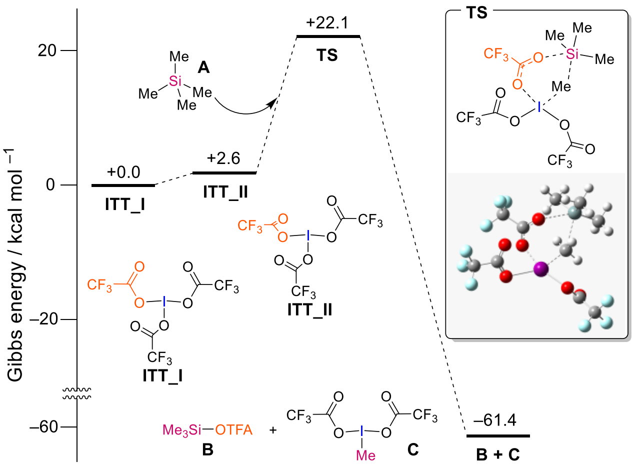
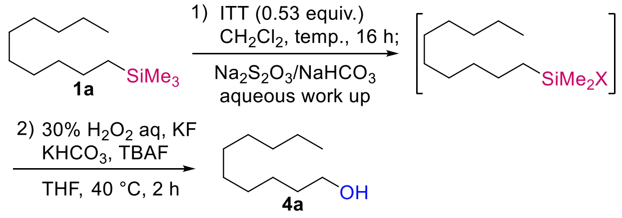


Figure 1. Gibbs free energy diagram for the reaction of Me_4Si (**A**) with ITT, calculated at the M06-2X/def2-TZVPPD+SMD(CH_2Cl_2)//M06-2X/def2-SVP level of theory.

Subsequently, we examined the reaction of tetraalkylsilanes with ITT followed by Tamao–Fleming oxidation using H_2O_2 to establish a method for the conversion of a trialkylsilyl group to a hydroxy group in larger organic molecules (Table 1). Treatment of decyltrimethylsilane (**1a**) with ITT in CH_2Cl_2 at room temperature and subsequent workup with an aqueous solution of $Na_2S_2O_3/NaHCO_3$ provided the decyldimethylsilyl

Table 1. Investigation of the Cleavage of the Si–C(sp^3) Bond in Decyltrimethylsilane (1a) with ITT[a]



entry	temp. (°C)	yield (%)[b]
1	r.t.	>95
2	−20	>95
3	−40	>95
4	−60	57

[a] Reaction conditions: (1) **1a** (0.05 mmol) and ITT (0.53 equiv) in CH_2Cl_2 (0.5 mL) for 16 h at the indicated temperature; (2) for details of the Tamao–Fleming oxidation, see the Supporting Information. [b] The yields of alcohol **4a** were determined by ^1H NMR analysis of the crude reaction mixtures using 1,1,2,2-tetrachloroethane as an internal standard.

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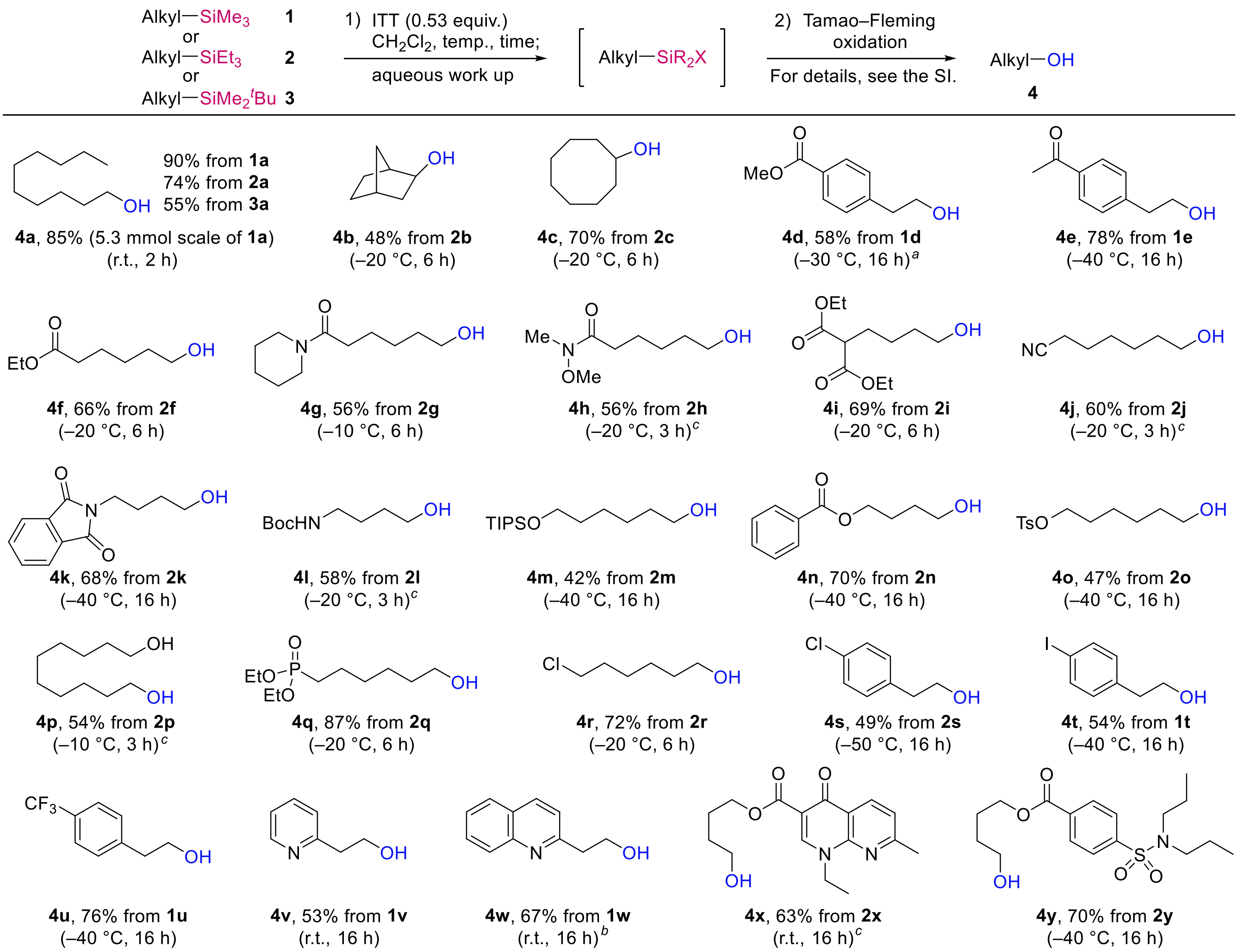
Scheme 3. Substrate Scope of Alcohol Synthesis through Cleavage of a Si−C(sp^3) Bond in Tetraalkylsilanes 1−3[d]

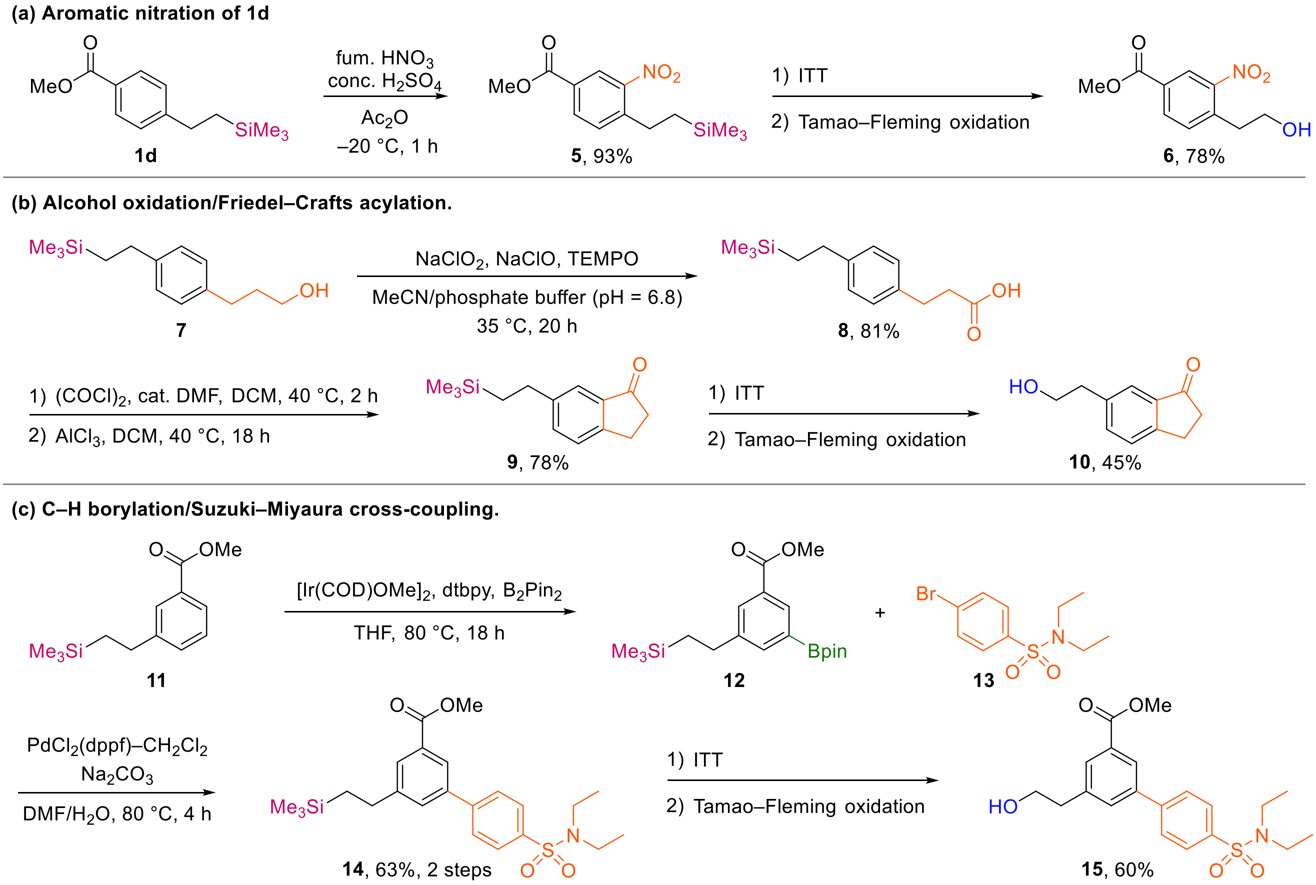


[a]ITT (0.50 equiv). [b]ITT (0.75 equiv). [c]With BF_3•OEt_2 (1.1 equiv) as an additive. [d]Reaction conditions: (1) **1**, **2**, or **3** (0.3 mmol) and ITT (0.53 equiv) in CH_2Cl_2 (3 mL), unless otherwise noted. The reaction temperature and time are shown in parentheses; (2) for details of the Tamao−Fleming oxidation, see the Supporting Information.

intermediate almost quantitatively via selective cleavage of the smallest alkyl group, i.e., the methyl group (for details, see Figure S3). This selectivity should probably be attributed to steric hindrance. This intermediate was then converted into the corresponding alcohol **4a** in high yield under Tamao−Fleming oxidation conditions using H_2O_2 and fluorides[14] (entry 1). ITT also reacted with **1a** at lower temperatures (entries 2−4), and the reaction proceeded in moderate yield even at −60 °C (entry 4). As control experiments, we examined the reactions of **1a** with several λ^3-iodanes and $I(OAc)_3$ instead of ITT. In these cases, no reaction proceeded even at room temperature (for details, see Scheme S1).

We applied the established method to various tetraalkylsilanes bearing functional groups (Scheme 3). In all cases, the product was isolated and characterized as the corresponding alcohol. In addition to the trimethylsilyl group (**1a**), a triethylsilyl group (**2a**) and *tert*-butyldimethylsilyl group (**3a**) were also converted into a hydroxy group in good to moderate yields. Although the cleavage of the Si−C(sp^3) bonds by ITT proceeded in high conversion, the steric hindrance of the silyl group may have reduced the reactivity of the subsequent Tamao−Fleming oxidation,[5d] leading to the observed lower yields of **4a** from **2a** and **3a** compared with **1a**. Secondary alkylsilanes also provided the corresponding secondary alcohols (**4b**, **4c**). Tetraalkylsilanes bearing a broad range of carbonyl groups, a cyano group, protected amines, and alcohols could also be used in this reaction by adjusting the reaction temperature (**1d**, **1e**, **2f**−**o**). Notably, an active methylene moiety, which often reacts with hypervalent iodine compounds,[15] was also tolerated (**2i**). In some cases (**2h**, **2j**, **2l**, **2p**, **2x**), electrophilic ethylation of the polar functional groups was observed, probably via an in situ-generated ethyl-λ^3-iodane as a strong electrophile. In situ protection of the Lewis basic functional groups of these substrates with BF_3·OEt_2 was effective in circumventing the competing alkylation and promoting chemoselective Si−C(sp^3) bond cleavage.[16] We successfully obtained the desired alcohols in the presence of acid-sensitive Boc and TIPS moieties (**4l**, **4m**) and an oxidizable free hydroxy group (**4p**), demonstrating the polar functional group tolerance of our method. Alkylsilanes containing a synthetically useful Weinreb amide or phosphonate moiety also afforded the corresponding alcohols (**4h**, **4q**)

Scheme 4. Application in the Multistep Synthesis of Functionalized Molecules[a]



[a]For detailed reaction conditions, see the Supporting Information.

in 56 and 87% yield, respectively. Some halogen substituents and nitrogen-containing heteroarenes were compatible with our method (**2r**, **2s**, **1t**−**w**). In addition, as multifunctionalized substrates, alkylsilanes derived from nalidixic acid and probenecid afforded the corresponding alcohols **4x** and **4y** in good yields. Moreover, we performed a large-scale reaction using 5.3 mmol of **1a** to afford the corresponding alcohol **4a** in 85% yield, demonstrating the scalability of our developed protocol. On the other hand, substrates with a terminal alkene or an electron-rich aryl moiety were unsuccessful because of competing reactions of such functional groups with ITT (Figure S4).[17]

To demonstrate the synthetic advantages arising from the high stability of tetraalkylsilanes, we investigated the application of the developed method in the multistep synthesis of functionalized molecules under various reaction conditions that could potentially affect less stable synthetic precursors for alcohols, such as organoborons (Scheme 4).[18] Initially, we examined the electrophilic aromatic nitration of tetraalkylsilane **1d** with fuming nitric acid and concentrated sulfuric acid in Ac_2O.[19] The reaction proceeded efficiently without protodesilylation or oxidation of the trimethylsilyl group to afford **5** in 93% yield. The synthesized tetraalkylsilane **5** was then converted into the corresponding alcohol **6** via ITT oxidation/Tamao−Fleming oxidation in 78% yield. Next, we oxidized primary alcohol **7** to carboxylic acid **8** in good yield using $NaClO_2$/NaClO/TEMPO.[20] Carboxylic acid **8** was further derivatized via acyl chloride formation and subsequent $AlCl_3$-mediated intramolecular Friedel−Crafts acylation to afford indanone **9**. In these transformations, the trimethylsilyl group remained intact. The tetraalkylsilane derived from indanone **9** was also converted into the corresponding alcohol **10**. Furthermore, we conducted an Ir-catalyzed C−H borylation[21] of the aryl ring in tetraalkylsilane **11** and subsequent Suzuki−Miyaura cross-coupling with aryl bromide **13** to obtain biaryl derivative **14** in good yield without loss of the trimethylsilyl group. Multifunctionalized biaryl **14** was also a suitable substrate for the developed method, affording alcohol **15** in 60% yield.

In summary, we have developed a method for the chemoselective cleavage of Si−C(sp^3) bonds in unactivated tetraalkylsilanes that contain several polar functional groups using iodine tris(trifluoroacetate). The application of this method to the multistep synthesis of functionalized molecules without loss of the trimethylsilyl groups demonstrated the synthetic utility of unactivated tetraalkylsilanes as inexpensive and highly stable masked alcohols. Our findings can be expected to induce further studies of the synthesis and utilization of tetraalkylsilanes in organic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11645.

Experimental procedures and spectral data for all new compounds (PDF)

Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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