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Light-driven silane functionalization using disulfide and dichloromethane

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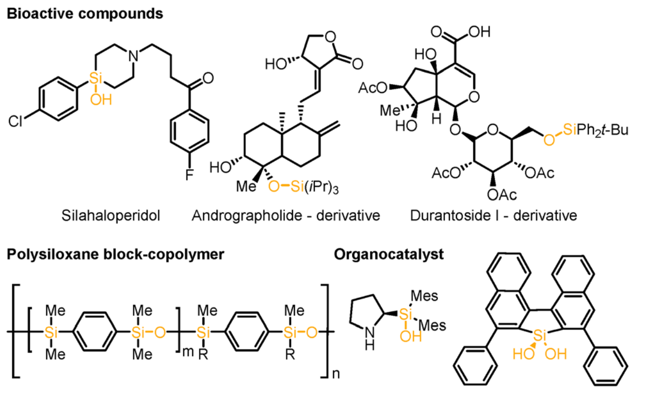
Organosilicon compounds are of great importance in material and synthetic chemistry. Herein, we disclose a practical and general silane functionalization protocol that enables direct access to silanols and silyl ethers. The process features mild, environmentally benign conditions and enables the transformation of diverse silanes into valuable organosilicon compounds.

Organosilicon compounds have been broadly utilized as valuable building blocks in material science[1] and organic synthesis (Scheme 1).[2] Among them, silanols and silyl ethers find wide applications in silicon-based materials, metallasiloxane synthesis,[3] C–H activation,[4] organocatalysis,[5] and medicinal chemistry.[6] Motivated by the applications of organosilicon compounds, research has been actively conducted in the field of organic synthesis to develop methods for synthesizing these compounds. These are typically achieved through the hydrolysis of silyl chlorides[7] or the oxidation of silanes with stoichiometric oxidants such as permanganate, osmium tetroxide, dioxirane, and ozone.[8] However, the hydrolysis of silyl chlorides often suffers from low efficiency owing to the condensation of silanols to siloxanes, while oxidation of silanes with theses reagents is limited by narrow substrate scope, poor functional group tolerance, and the generation of substantial waste. To address issues, transition-metal-catalyzed[9] or photocatalytic[10] methods have emerged as an attractive approach. However, most reported methods rely on noble metal catalysts and often suffer from the undesired formation of disiloxanes, arising from competitive reactions of silanols with hydrosilanes (Fig. 1A). In 2019, Wu and co-workers disclosed a photocatalytic method employing eosin Y, where hydrosilanes undergo chlorination and subsequent reaction with alcohols to afford the corresponding silyl ethers (Fig. 1B).[11] Although significant progress has been made, practical and robust methods for accessing silanols and silyl ethers still limited. We hypothesized that the *in situ* generation of silyl chlorides from silanes under mild conditions would provide a versatile precursor, enabling their subsequent conversion into silanols and silyl ethers through reaction with oxygen nucleophiles.

Herein we report a practical, photocatalyst-free method for silane functionalization using disulfides and dichloromethanes under purple light irradiation (Fig. 1C). In our design, thiyl radicals were generated *in situ* from disulfides without the need for additional catalysts and efficiently engaged in hydrogen atom transfer (HAT) to form silyl radicals.[12] The resulting silyl radicals then underwent halogen atom transfer (XAT) with dichloromethane, thereby furnishing silyl chlorides under mild conditions. Furthermore, the *in situ* generated silyl chlorides can be selectively converted into either silanols (with water) or silyl ethers (with alcohols), offering modular access to multiple classes of valuable organosilicon compounds from the same hydrosilane precursor. This method provides an environmentally benign alternative to existing photocatalytic approaches, relying exclusively on inexpensive commercial reagents and expanding the synthetic utility of hydrosilanes.

We started our investigation of silanol synthesis using diphenylmethyl silane (**1a**) as a model substrate. After the



Scheme 1 Useful organosilicon compounds.

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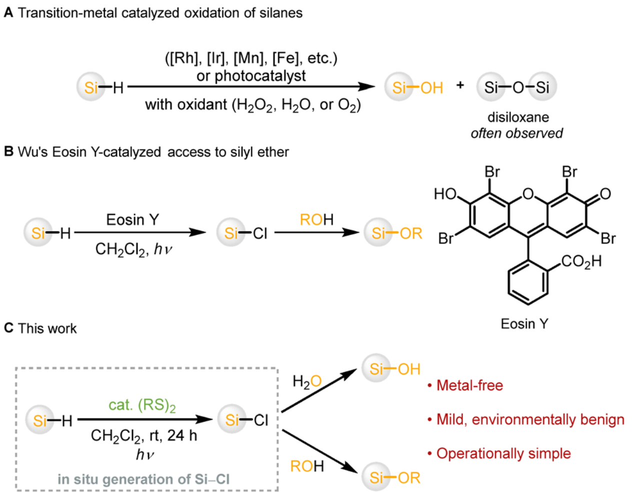
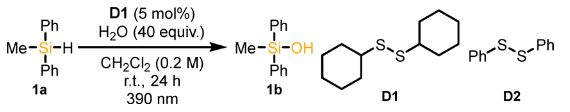


Fig. 1 Previous works and this work. (A) Transition-metal catalyzed oxidation of silanes. (B) Wu's Eosin Y-catalyzed access to silyl ether. (C) This work.

systemic screening, the optimal conditions were obtained as follows (see SI for further information): **1a** (1.0 equiv.), dicyclohexyl disulfide (**D1**, 20 mol%), H_2O (40 equiv.) in a solution of CH_2Cl_2 at room temperature under 390 nm irradiation for 24 hours (Table 1, entry 1). Under these conditions, the desired silanol **1b** was obtained in 72% isolated yield. Based on this result, several control experiments were conducted. Reducing the disulfide loading from 5 mol% to 1 mol%, the reaction efficiency was significantly dropped (entry 2). Additionally, diphenyl disulfide (**D2**) was not efficient for product formation due to the low BDE of aryl thiols (*ca.* 79 kcal mol^{-1}) (entry 3).[13] When CH_2Cl_2 was replaced with other chlorine sources, including *n*-BuCl or 1,2-dichloroethane (DCE) or CH_3Cl, the yield decreased significantly (entry 4–6). Replacing 390 nm with 440 nm did not afford the desired product (entry 7). Without water, only trace amounts of silanol were observed, while silyl chloride was obtained in 82% yield (entry 8).

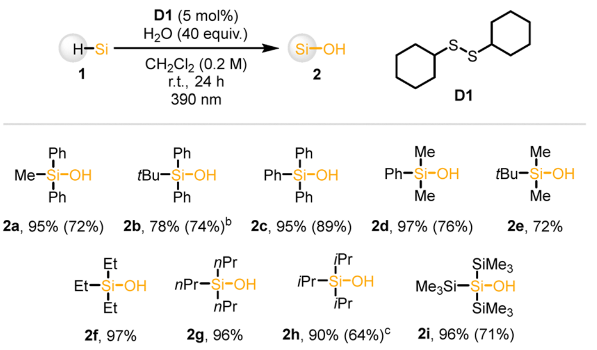
Table 1 Control experiments



Entry	Deviation from standard conditions[a]	Yield[b] [%]
1	None	97 (72[c])
2	1 mol% of **D1**	3
3	**D2** instead of **D1**	8
4	*n*-Bucl instead of CH_2Cl_2	10
5	DCE instead of CH_2Cl_2	38
6	$CHCl_3$ instead of CH_2Cl_2	43
7	440 nm instead of 390 nm	Trace
8	Without H_2O	Trace[d]

[a] Reaction conditions: **1a** (0.2 mmol), **D1** (5 mol%), H_2O (40 equiv.), CH_2Cl_2 (0.2 M), 390 nm irradiation at r.t. for 24 h. [b] Yield was determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] Isolated yield. [d] Silyl chloride was obtained.

Table 2 Substrate scope for synthesis of silanols[a]

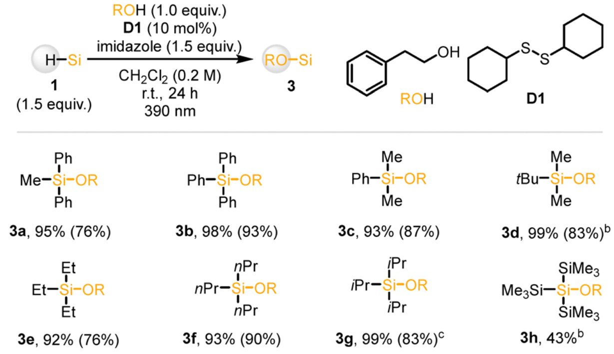


[a] Reaction conditions: **1** (0.2 mmol), **D1** (5 mol%), H_2O (40 equiv.) in DCM (0.2 M) at r.t. under 390 nm irradiation. [b] 48 h. [c] Addition of 1.5 equiv. of imidazole for 72 h. Yield determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard; isolated yields are shown in parentheses.

With the optimized conditions in hand, various silanes were investigated to access corresponding silanols (Table 2). In general, a broad range of silanes bearing aryl, alkyl, and silyl substituents were smoothly converted into the corresponding silanols. Mono-, di- and triaryl substituted silanes afforded the desired product (**2a–2d)** with high yield. In addition, trialkylsilanes including *t*BuMe$_2$SiH, Et$_3$SiH, and *n*Bu$_3$SiH, were well tolerated, giving the excellent yield (**2e–2g**). Plus, sterically demanding iPr$_3$SiH furnished silnaol **2h** in 87% yield. Furthermore, tris(trimethylsilyl)silane (supersilane) also underwent smooth conversion to the silanol in 96% yield (**2i**), highlighting generality of this protocol.

Encouraged by the success of silanol formation, we sought to extend the protocol to the synthesis of silyl ethers using alcohols as nucleophiles. Reaction optimization revealed that the presence of alcohols together with silanes (1.5 equiv.) and with 1.5 equiv. of imidazole afforded corresponding silyl ethers (see SI for further optimization, Table S5). As shown in Table 3,

Table 3 Substrate scope for synthesis of silyl ethers[a]



[a] Reaction conditions: 2-phenylethanol (1.0 equiv.), **1** (1.5 equiv.), imidazole (1.5 equiv.) **D1** (5 mol%) in CH_2Cl_2 (0.2 M) at r.t. under 390 nm irradiation. [b] 48 h. [c] 72 h. Yield determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard; isolated yields are shown in parentheses.

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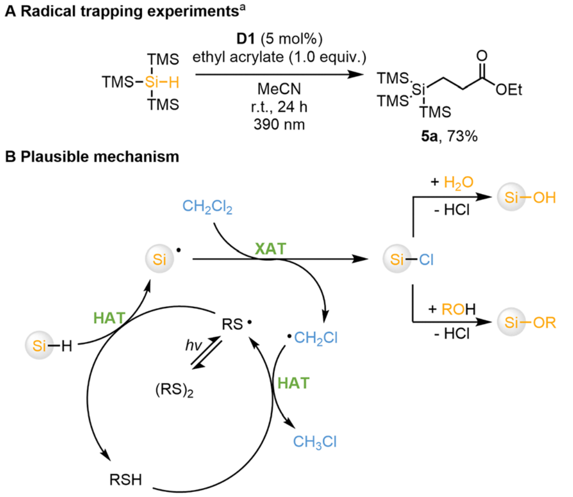

Fig. 2 (A) Radical trapping experiments. ^{a}Tris(trimethylsilyl)silane (1.0 equiv.), **D1** (5 mol%), ethyl acrylate (1.0 equiv.) in MeCN (0.2 M) at r.t. under 390 nm irradiation. (B) Plausible mechanism.

a wide range of silanes were compatible with this transformation, providing the desired silyl ethers. Several aryl-substituted silanes gave silyl ether with excellent yield (**3a–3c**). Also, trialkyl substituted silyl ether (**3d–3g**) were obtained in high yields. Additionally, supersilane underwent smooth transform to provide **3h** in a moderate yield.

Mechanistic studies were carried out to elucidate reaction mechanism (Fig. 2). Radical trapping experiments using ethyl acrylate resulted in the formation of the corresponding hydrosilylation product (**5a**), providing direct evidence for the generation of a silyl radical intermediate under the photochemical conditions (Fig. 2A). A plausible mechanism for this reaction is proposed in Fig. 2B. Under 390 nm purple light irradiation, the S–S bond in dicyclohexyl disulfide undergoes homolytic cleavage,[13] generating thiyl radicals to produce a silyl radical through HAT. The silyl radical can undergo XAT with dichloromethane to generate silyl chloride. In the presence of H_2O or alcohol, the reaction furnishes the corresponding silanol or silyl ether. The resulting chloromethyl radical can abstract a hydrogen atom from thiol, thereby generating a thiyl radical and propagating the radical chain.

In conclusion, we have developed a simple and general method for functionalization of silanes using commercially available and environmentally benign reagents. This transformation proceeds under mild reaction conditions to produce various organosilicon compounds including silanols, silyl ether, and silyl chlorides. We believe this transformation offers a valuable platform for future applications in organosilicon chemistry and related fields.

H. K. and J. L. designed and carried out the experiments. J. L. and S. L. wrote the manuscript. S. L. supervised the project.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information (SI). Supplementary information includes experimental procedures, characterization data, and NMR spectra. See DOI: https://doi.org/10.1039/d6cc00213g.

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