

Si–H Activation

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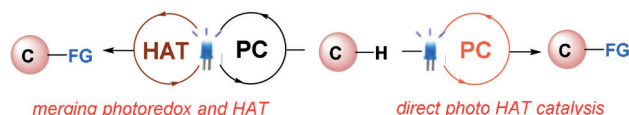
Neutral-Eosin-Y-Photocatalyzed Silane Chlorination Using Dichloromethane

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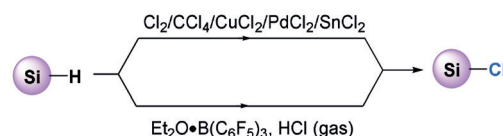
Abstract: Chlorosilanes are versatile reagents in organic synthesis and material science. A mild pathway is now reported for the quantitative conversion of hydrosilanes to silyl chlorides under visible-light irradiation using neutral eosin Y as a hydrogen-atom-transfer photocatalyst and dichloromethane as a chlorinating agent. Stepwise chlorination of di- and trihydrosilanes was achieved in a highly selective fashion assisted by continuous-flow micro-tubing reactors. The ability to access silyl radicals using photocatalytic Si–H activation promoted by eosin Y offers new perspectives for the synthesis of valuable silicon reagents in a convenient and green manner.

Photoinduced catalytic hydrogen-atom transfer (HAT) can activate substrates without the limitation of redox potentials, and has provided enormous opportunities for C–H activations.^[1] A photoredox catalyst and a HAT mediator are normally involved in these reactions, where a reactive species is generated by photopromoted single-electron oxidation of the mediator for the subsequent hydrogen atom abstraction. A more reagent- and redox-economical strategy is by employing the direct photo HAT catalyst, which can directly abstract the hydrogen atom after assimilating a photon, omitting the redox activation step (Scheme 1a).^[1] Photo-induced direct HAT catalysis has endowed with a wide range of reaction patterns to allow C–H functionalization.^[2] However, Si–H activation has rarely been investigated as a means of synthesizing value-added silicon compounds through the use of modern photocatalysis strategy.^[3] As silicon is more electropositive than carbon (electronegativity of 1.90 vs. 2.55 on the Pauling scale), Si–H bonds are generally more hydridic than C–H bonds. In this context, we have recently achieved a visible-light mediated hydrosilylation of both electron-deficient and electron-rich alkenes through the synergistic merger of a photoredox catalysts and a HAT

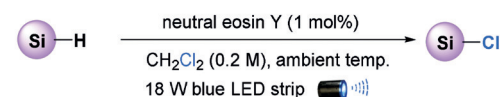
a) Photo-induced HAT for C–H activation



b) Established chlorination of Si–H bonds



c) Visible-light mediated chlorination of silanes (this work)



- metal-free
- ambient conditions
- visible-light-mediation
- additive-free
- CH₂Cl₂ as Cl source as well as solvent

Scheme 1. Chlorination of hydrosilanes through photoinduced HAT.

mediator.^[4] Additionally, we recently disclosed the unique property of neutral eosin Y, which can function as an ideal direct HAT photocatalyst owing to its visible-light-absorption, metal-free, readily available, and low-cost nature.^[5] It has been applied to the C–H alkylation, which accommodates an extremely broad substrate scope owing to no limitation on redox potentials.^[5] In view of the electrophilic nature of the oxygen radical in the photoexcited eosin Y triplet state, it was anticipated that this catalytic HAT procedure might be extended to abstraction of protons from hydridic Si–H bonds, to access transient and reactive silyl radicals for the synthesis of value-added silicon reagents.^[6]

Chlorosilanes are widely used reagents in organic chemistry and material science. They are extensively utilized in multistep organic synthesis for the installation of silyl protecting groups on alcohols, amines, acids, and alkynes.^[7] They are also applied in the preparation of silyl metallic reagents or silyl enol ethers to access hard or soft nucleophiles.^[8] Chlorosilanes are extensively involved in the production of silicon-based polymers,^[9] and coating for silicon and glass surfaces.^[10] However, the synthesis of chlorosilanes by chlorination of Si–H bonds normally requires stoichiometric amounts of metal salts in conjunction with hazardous chlorine reagents, such as tin chloride, lead chloride, Cl₂, and CCl₄, or the use of expensive transition-metal catalysts (Scheme 1b).^[11] Notably, Dobrovetsky et al. recently reported a B(C₆F₅)₃-catalyzed selective chlorination of hydro-

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silanes using HCl as the chlorinating agent.^[12] However, a large excess gaseous HCl was employed in this method in an uncontrollable way. Consequently, the development of an operationally simpler and green catalytic procedure for chlorinating of hydrosilanes is appealing and highly desirable. Herein, we describe a green and selective method to generate chlorosilanes through neutral eosin Y-catalyzed HAT with hydrosilanes under visible-light irradiation using dichloromethane (DCM) as both the chlorinating agent and solvent (Scheme 1c). Different from the industrial Müller–Rochow process to catalytically prepare chlorosilanes using alkyl halides and elemental silicon at high temperature (for example, 300 °C),^[13] our method provides a convenient and complementary way to access chlorosilanes from hydrosilanes at a laboratory scale.

Our initial investigation showed that treatment of diphenylmethyl silane (**1**) in dichloromethane in the presence of 1 mol % neutral eosin Y under blue LED irradiation ($\lambda_{\text{max}} = 470 \text{ nm}$, 18 W), produced a quantitative yield of diphenylmethylchlorosilane (**2**) (Table 1, entry 1). Dichloromethane is

Table 1: Investigation of reaction parameters for silane chlorination.^[a]

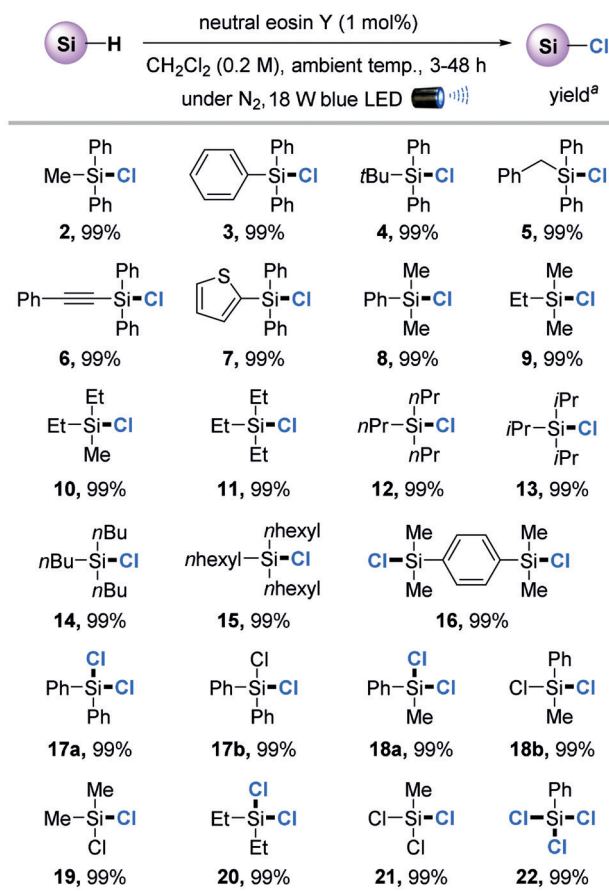
Entry	Deviation from standard conditions ^[a]	Yield [%] ^[b]
1	none	99
2	CHCl ₃ instead of CH ₂ Cl ₂	85
3	ClCH ₂ CH ₂ Cl instead of CH ₂ Cl ₂	67
4	CH ₂ Cl ₂ (0.5 M)	71
5	Ru(bpy) ₃ (PF ₃) ₂ instead of eosin Y	0
6	ionic eosin Y instead of neutral eosin Y ^[c]	0
7	with air balloon	31
8	adding TEMPO (2.0 equiv)	0
9	no photocatalyst or no light	0

[a] Standard conditions: **1** (1 mmol), neutral eosin Y (1 mol %) and CH₂Cl₂ (5 mL) under N₂ in a 10 mL seal vial, irradiated under 18 W blue LED for 4 h at ambient temperature. [b] Yields determined by analysis of the crude ¹H NMR using CH₂Br₂ as an internal standard. [c] Irradiated using an 18 W white LED strip.

widely utilized as chlorinated solvent in pharmaceutical chemistry, which has been proposed as a replacement for other chlorinated solvents in cases when a chlorine-free solvent is not applicable.^[14] It acted as both a chlorine source and solvent media in our procedure, avoiding the usage of hazardous chlorinated reagents. The reaction became less efficient when dichloromethane was replaced by chloroform or dichloroethane (DCE; entries 2 and 3). A lower efficiency was also detected in more concentrated dichloromethane solution (entry 4). Notably, employment of Ru(bpy)₃(PF₃)₂ as the photocatalyst, which possesses redox properties similar to those of eosin Y, failed to produce any of the desired product (entry 5). No transformation was observed using the commercial dianionic form of eosin Y as the photocatalyst (entry 6), and this is consistent with our previous recognition of neutral eosin Y as the active HAT photocatalyst.^[5] The yield of chlorosilane decreased significantly in the presence of

air (entry 7), which led to production of siloxane by-products. The reaction was suppressed in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), suggesting a radical-based process (entry 8). Control experiments demonstrated that light and the photocatalyst were both essential for efficient chlorination (entry 9).

The generality of silane chlorination was evaluated by employing the optimal reaction conditions (Table 1, entry 1). As depicted in Scheme 2, aryl-substituted silanes, including tri-, di-, and mono-aryl silanes with different steric properties, were well-tolerated and afforded the corresponding chlorosilanes (**2–8**) quantitatively. Trialkylsilanes with different

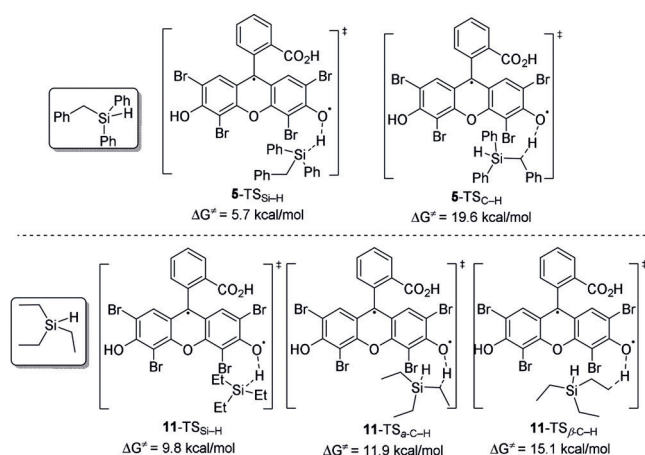


Scheme 2. Scope of silane chlorination. [a] Reactions performed on a 1 mmol scale in 5 mL CH₂Cl₂. Yields were determined by analysis of the crude ¹H NMR using dibromomethane as an internal standard.

sized alkyl groups performed effectively to give the corresponding products (**9–15**) in excellent yields. Disilanes such as *para*-phenylenebis(dimethylsilane) were also effective substrates, smoothly delivering the dichlorinated product (**16**). The dichlorosilanes (**17–20**) could be quantitatively generated by chlorination of either R¹R²SiH₂ or the mono-chlorosilane, R¹R²SiClH. Dichloromethylsilane delivered methyltrichlorosilane (**21**) smoothly. Phenylsilane was a good candidate in this procedure and produced phenyltrichlorosilane (**22**). In contrast to tetrabutylammonium decatungstate-catalyzed hydrosilylation under UV light irradiation, in which a mixture

of the Si–H and C–H activation products were obtained,^[6] the eosin Y-catalyzed procedure demonstrated an excellent selectivity of Si–H activation in the presence of activated C–H bonds, such as benzylic and α -silyl C–H bonds.

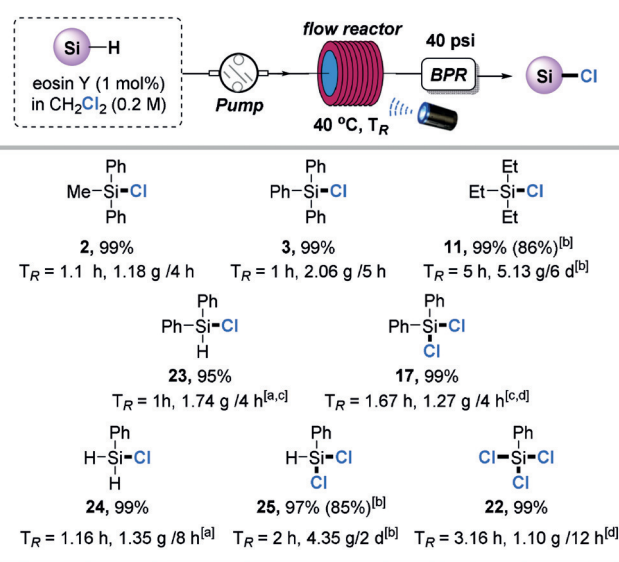
DFT calculations (see the Supporting Information for details)^[15] of transition states for hydrosilane HAT with light-activated eosin Y at various sites were conducted to probe the kinetic origins of selectivity. As illustrated in Scheme 3, the calculated activation energies revealed an appreciable kinetic preference for abstraction of Si–H rather than the benzylic and α -silyl C–H bonds by the photo-activated eosin Y.



Scheme 3. Calculated relative activation energies (ΔG^\ddagger) for HAT with photo-activated eosin Y.

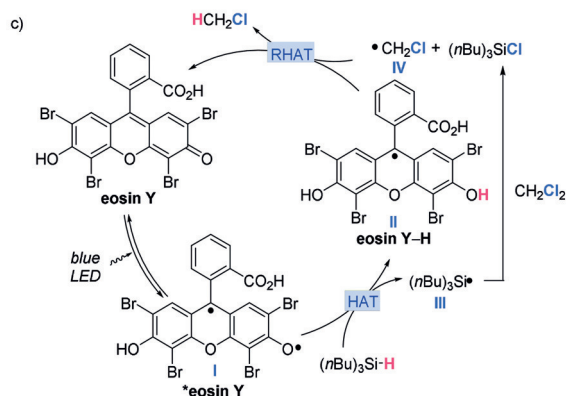
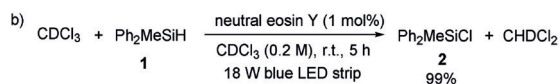
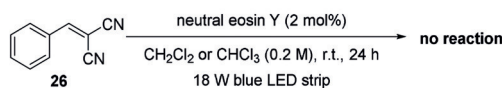
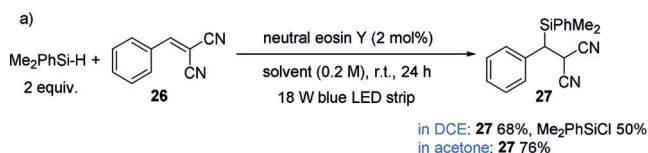
Compared to stirred reactor vessels, continuous-flow micro-tubing reactors have significant processing advantages, including improved mass/heat transfer and mixing efficiency, and precise control of residence time.^[16] They provide an excellent platform for photochemical reactions owing to the enhanced and uniform light irradiation and ease of scaling up.^[17] As demonstrated in Scheme 4, the silane chlorination assisted by an operationally simple continuous-flow micro-tubing reactor was amenable to gram-scale production (**2,3,11**). More intriguingly, stepwise chlorination of di- and trihydrosilanes ($R^1R^2SiH_2$ and $RSiH_3$) was successfully achieved in a highly selective manner (**23** vs. **17**; **24** vs. **25** vs. **22**). Compared to the dramatically reduced selectivity obtained in batch stirred reactors (Supporting Information, Scheme S4), the key to success relied on the excellent mixing efficiency and precise control of reaction temperature and residence time associated with continuous-flow micro-tubing reactors.^[16]

To gain further insight into the nature of the chlorination, several control experiments were performed. Reaction monitoring by UV/Vis spectroscopy (Supporting Information, Figure S7) confirmed that the neutral eosin Y species was the active photocatalyst during the reaction process.^[5] Hydrosilylation product **27** was generated in good yields with the same photocatalytic system by addition of alkene **26** in either acetone or DCE, while no reaction was observed in the absence of silanes (Scheme 5a), which supported the generation of silyl radicals in different solvents. This eosin Y-based



[a] Flow reactions conducted at 30 °C. [b] Isolated yields after purification by distillation. [c] in CH_2Cl_2 (0.3 M). [d] Flow reactions conducted at 50 °C.

Scheme 4. Gram-scale and stepwise chlorination in continuous-flow micro-tubing reactors.



Scheme 5. Proposed mechanism and supporting evidence.

photocatalytic procedure is therefore one of the most mild and convenient methods to introduce silyl radicals from hydrosilanes. When the silane chlorination was performed in deuterated chloroform, mono-deuterated DCM ($CDHCl_2$) was clearly detected in the 1H NMR spectra of the crude reaction mixture (Scheme 5b; Supporting Information, Figure S13). Luminescence quenching studies (Supporting Information, Figure S8) indicated that the Si–H activation was not

induced by either an electron- or an energy-transfer process. The HAT process was further supported by laser flash photolysis experiments. Upon laser excitation at 532 nm, a new absorption peak emerged after 30 μ s at 360 nm after addition of silanes in eosin Y CH_2Cl_2 and MeCN solution, which was not observed in the absence of silanes (Supporting Information, Figures S10 and S11). It was corresponding to the radical intermediate of eosin Y–H generated from HAT between *eosin Y and the silane.^[5] Both light on/off experiments (Supporting Information, Figure S12) and the calculated quantum yield ($\Phi = 0.35$) suggested a nonchain pathway.^[18]

In light of all the experimental data, a plausible mechanism is proposed (Scheme 5c). The silyl radical **III** is generated smoothly by the HAT between light-activated *eosin Y (**I**) and hydrosilane. The formation of an intermediate eosin Y–H (**II**) was confirmed by laser flash photolysis experiments. The derived silyl radical subsequently abstracts the chloride from DCM to deliver the silyl chloride product and the chloromethyl radical species (**IV**). A reverse hydrogen atom transfer (RHAT) between radical **IV** and eosin Y–H (**II**) regenerates ground state eosin Y and produces chloromethane, which was detected by ^1H NMR analysis of the crude reaction mixture. Based on DFT calculations, the RHAT process has an energy barrier of 11.8 kcal mol $^{-1}$, which is significantly lower than the 37.4 kcal mol $^{-1}$ associated with a single electron transfer pathway between **II** and **IV** (Scheme S1; Supporting Information, Figures S4 and S5).

The synthetic value of this straightforward photo-mediated silane chlorination was further demonstrated by one-pot synthesis of various types of valuable compounds. As illustrated in Scheme 6, the crude DCM solution of silane chlorination could be directly utilized in subsequent transformations for silanol synthesis (path a), alcohol protection (path b), silyl enol ether formation (path c), silylation of nitroalkanes (path d), alkyne protection (path e), and phenyl

silylation (path f), achieving products in good to excellent yields in all cases.

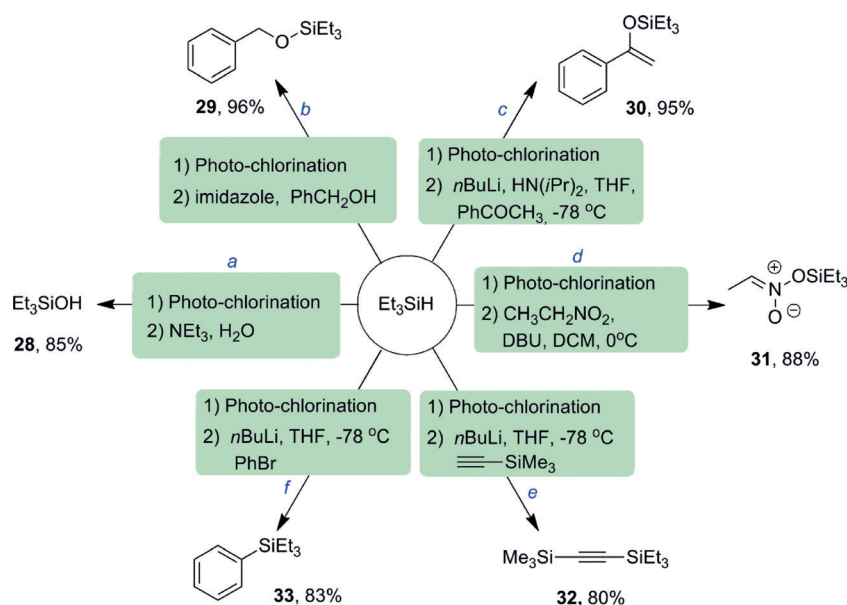
In conclusion, we have developed a visible-light-mediated silane chlorination catalyzed by neutral eosin Y, using DCM as both a chlorinating agent and the solvent media. This transformation accommodates a wide range of silanes, achieving products with exclusive Si–H activation in the presence of activated C–H bonds. This procedure is also distinguished by its operational simplicity, metal-free character, use of ambient conditions, green reagents, and delivery of quantitative yields in most cases, and can be directly streamlined with a sequential transformation. A highly selective stepwise chlorination of di- and trihydrosilanes was achieved assisted by the unique advantages of continuous-flow micro-tubing reactors. More importantly, the neutral eosin Y-based HAT provides a very convenient and green approach for the generation of silicon radicals under visible-light irradiation, which promise to find wide applications in the synthesis of valuable silicon compounds in both academic and industrial settings.

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Conflict of interest

The authors declare no conflict of interest.



Scheme 6. Synthetic utility of silane chlorination.

Keywords: dichloromethane · hydrogen atom transfer · neutral eosin Y · Si–H activation · silyl chloride

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