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Visible-Light Induced Radical Silylation for the Synthesis of Dibenzosiloles via Dehydrogenative Cyclization

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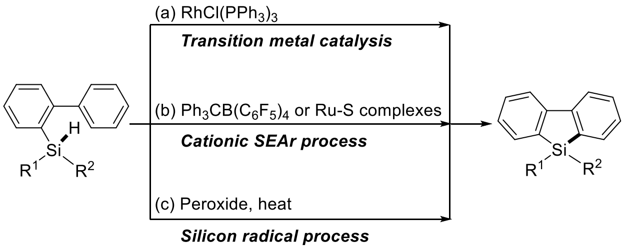
Abstract. A visible-light induced radical silylation to dibenzosiloles from biarylhydrosilanes is described. The products were obtained in satisfactory yields under mild and water/air compatible conditions, providing an efficient and practical method for the synthesis of difunctionalized siloles by using a cheap organic dye photocatalyst. The method is tolerated by a wide range of functional groups and has a broad substrate scope. Light/dark experiments and quantum yield measurements provided support for a photocatalytic pathway rather than a chain process.

Keywords: Visible Light Photoredox Catalysis; Dibenzosilole; C-Si bond formation; Radical reaction

Dibenzosilole (9-silafluorene) derivatives have attracted much attention due to their applications in organic electronic and photonic materials, such as light emitting materials, field effect transistors, photovoltaic cells, and fluorescent sensors.[1] Conventional methods to synthesize dibenzosiloles by metal−halogen exchange involve highly reactive organometallic reagents.[2] Recently, many transition-metal-catalyzed couplings or cycloadditions to synthesize diverse dibenzosiloles were developed employing rhodium,[3] palladium[4,5,6] and iridium catalysis.[7] However, these methods require pre-functionalized precursors such as halides, triflates or boronic acids, or complicated diynes. In comparison, the construction of C-Si bond *via* (formal) dehydrogenative coupling between a C–H bond and a Si–H bond is conceivably the most efficient approach (Scheme 1).[8] To this end, three different approaches have been reported: (a) the rhodium catalyzed C-H/Si-H coupling reactions reported by the Takai and He groups (Scheme 1a);[9] (b) the strong Lewis acid $B(C_6F_5)_3$ or cationic Ru-S complexes induced electrophilic aromatic substitution reactions (SEAr) reported by the Kawashima, Ingleson and Oestreich groups (Scheme 1b);[10] and (c) the homolytic aromatic substitution reactions involving silicon-centered radicals generated under heating reported by the Studer and Li groups (Scheme 1c).[11]

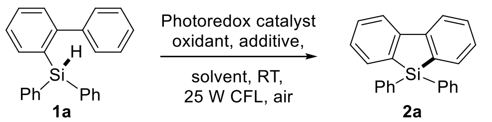


Scheme 1. Known (formal) dehydrogenative strategy.

Recently, visible-light photoredox catalysis has emerged as one of the most flourishing and attractive tools for organic transformations owing to its intrinsic characteristics of sustainability and mild operating conditions.[12] Although it has been well demonstrated that visible-light photoredox catalysis was quite effective for the construction of C–C,[13] C–N,[14] and C-O[15] bonds under mild conditions,[16] to the best of our knowledge, construction of C-Si bonds *via* visible-light photoredox catalysis still remains scarce.[17] Very recently, Wu reported a convenient visible-light-driven metal-free hydrosilylation of alkenes that proceeds through selective hydrogen atom transfer.[17a] While decatungstate-photocatalyzed hydrosilylation of electron-poor alkenes with silane was reported by Fagnoni group, the reaction was irradiated under UV light.[17b] The successful employment of visible-light photoredox catalysis[18] in C-Si bond formation would provide more efficient and green processes for the syntheses of silicon containing compounds.[19] Herein, we report a new, cost-effective, and powerful protocol for the preparation of dibenzosiloles *via* visible-light photoredox catalysis. Notable features of our findings include (i) C-Si bond formation *via* visible-light photoredox catalysis, (ii) cheap organic dye as the photoredox catalyst, (iii) mild and water/air compatible conditions, (iv) triflate group compatible conditions, (v) orthogonally difunctionalized silole can be obtained directly.

We commenced our study with biarylhydrosilane **1a** as the model substrate and surveyed photoredox

Table 1. Optimization of the reaction conditions[a]



Entry	Photocatalyst	Additive	Solvent	Yield (%)[b]
1	acridine	—	DMF	0
2	fluorescein	—	DMF	0
3	methylene blue	—	DMF	0
4	eosin Y-2Na	—	DMF	12
5	rose bengal	—	DMF	18
6	Ru(bpy)$_3$Cl$_2$	—	DMF	<5
7	Ru(bpy)$_3$PF$_6$	—	DMF	<5
8	rose bengal	—	DMSO	12
9	rose bengal	—	DME	10
10	rose bengal	—	CH_3OH	10
11	rose bengal	—	CH_3CN	14
12	rose bengal	—	DCE	22
13[d]	rose bengal	—	DCE	24
14	rose bengal	Cs_2CO_3	DCE	28
15	rose bengal	2,4-Lutidine	DCE	<5
16	rose bengal	KOH	DCE	40
17	rose bengal	*t*-BuOLi	DCE	30
18	rose bengal	CsOAc	DCE	26
19	rose bengal	KOH	DCE(H_2O-3 eq.)	40
20	rose bengal	KOH	DCE(H_2O-6 eq.)	42
21	rose bengal	KOH	DCE(H_2O-10 eq.)	44
22	rose bengal	KOH	DCE:H_2O= 2:1	70(65)[c]
23	rose bengal	KOH	DCE:H_2O= 1:1	67
24[e]	**rose bengal**	**KOH**	**DCE:H_2O= 2:1**	**81(77)[c]**

[a] The reaction was carried out with **1a** (0.2 mmol), TBHP (3.5 eq.), additive (2 eq.), solvent (3 mL), 36 h, irradiated with a 25 W CFL (one side; CFL = compact fluorescent light) under air and at room temperature.

[b] NMR yield.

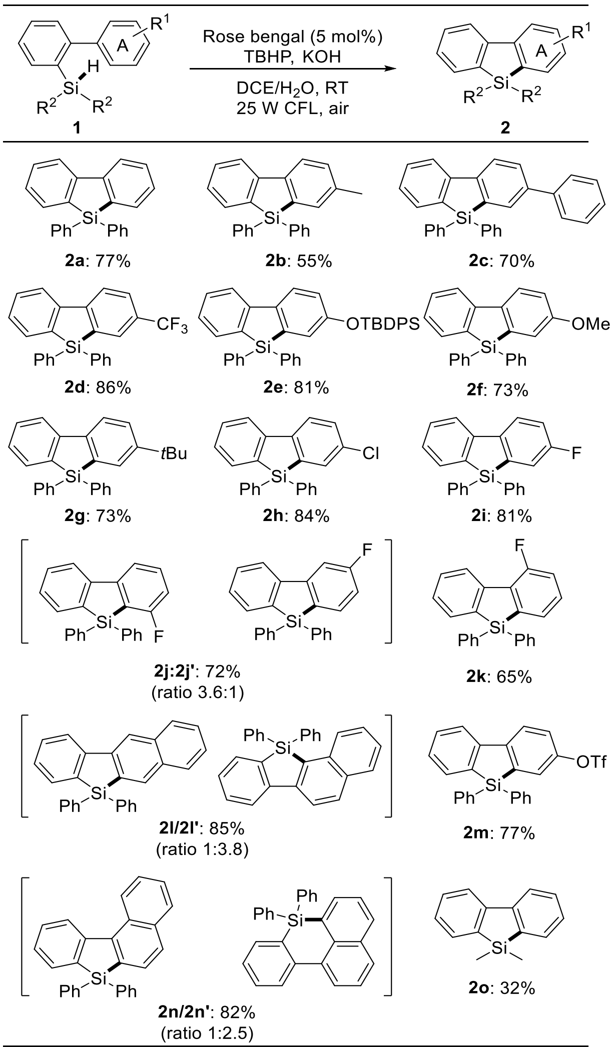
[c] Isolated yield.

[d] Conditions: anhydrous DCE (water <30 ppm), 4 Å molecular sieves, and N_2 atmosphere.

[e] Irradiated with 2 x 25 W CFL (both sides). TBHP = tert-butyl hydroperoxide.

catalysts, solvents, and bases (Table 1). Using DMF as the solvent, no reaction took place with acridine, fluorescein, and methylene blue (entries 1-3). Gratifyingly, the desired product **2a** was obtained in the presence of eosin Y-2Na or rose bengal (entries 4-5), albeit in low yields (12% and 18% repectively). The target product could also be observed with Ru photocatalyst, although a large amount of starting materials remained unreacted (entries 6-7). In order to improve the conversion and yield, solvents were then screened (see Supporting Information for the detailed study). DMSO, DME, CH_3OH, or MeCN made no improvements (entries 8-11). With DCE, the conversion of **1a** was improved dramatically. However, a significant amount of by-product silanol was obtained, which might come from trace amount of water (entries 12).[10d] To suppress this side reaction, anhydrous DCE (water < 30 ppm), molecular sieves, and Schlenk techniques were applied, however there were no noticeable benefit (entry 13). Considering the effect of base on the deprotonation step, further optimization was focused on the base additives (entries 14-18). The assumption was proved successful by using KOH and *t*-BuOLi as the base, which not only delivered the desired product **2a** in higher yields, but also suppressed the side reaction (entries 16-17). However, no improvements were obtained with stronger bases, such as *t*-BuONa, and *t*-BuOK (not shown). After extensive experimentation, the optimal conditions were found by using mixed solvents of DCE and H_2O (entries 19-24). Contrary to our understanding that the presence of water led to the formation of byproduct silanol,[20] the addition of H_2O in 1:2 ratio with DCE increased the yield to 70% with only trace amount of silanol formed (entry 22). The abundance of light was also important for the reaction, which further advanced the isolated yield of **2a** to 77% (entry 24).

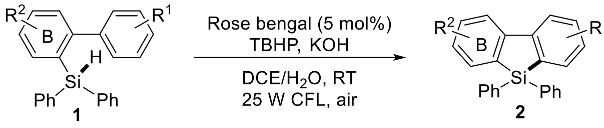
Table 2. Scope of substituted biarylhydrosilanes (ring A)[a]

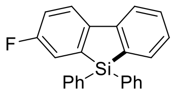


[a] Reaction conditions: **1** (0.2 mmol), rose bengal (0.05 eq.), TBHP (3.5 eq.), KOH (2 eq.), DCE/H_2O = 2:1 (v:v, 3 mL), irradiated with 2 x 25 W CFL (both sides) for 36 h under air and room temperature.

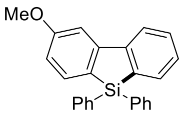
With the optimized conditions in hand, the visible-light induced radical silylation was applied to a wide scope of biarylhydrosilane substrates (Table 2). First, substituents on aryl ring A were examined. Biarylhydrosilanes bearing electron-donating and electron-withdrawing groups at the 4’-position gave the desired dibenzosiloles in moderate to excellent yields (**2b**‑**2i, 2m**). Overall, the 2-biarylhydrosilanes with electron-withdrawing trifluoromethyl (**2d**), halogen (**2h**, **2i**), triflate (**2m**) groups usually gave better yields than those with electron-donating groups such as methyl (**2b**), methoxyl (**2f**), and *t*-butyl (**2g**). The yields of the target products were also influenced by the position of functional groups. The 2’-fluoro substituted biarylhydrosilanes gave the desired product **2k** in 65% yield, while 3’ and 4’-fluoro substituted dibenzosiloles could be obtained in 72% and 81% yield, respectively. For meta-fluoro system and naphthalene ring systems, similar regioselectivity was observed as in Studer’s studies,[11a] but higher yields could be achieved under the visible-light photoredox conditions (**2j**, **2l**, **2n**). To our delight, precursors with oxygen donor, such as silicon-protected hydroxy group, could deliver the corresponding product **2e** in 81% yield. It is worth emphasizing that substrate with a triflate group, which could directly undergo a series of cross-coupling reactions, showed excellent compatibility with the visible-light photoredox conditions and gave **2m** in 77% yield comparing to the low conversion under Oestreich's conditions. Furthermore, other substituents on the silicon center were also tested. Not surprisingly, the di-methyl substituted silane delivered the corresponding product **2o** in much lower yield probably due to their less effective stabilizing effect on the silicon radical than phenyl groups.

Table 3. Scope of substituted biarylhydrosilanes (ring B, or both rings)[a]

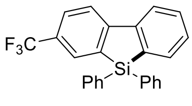




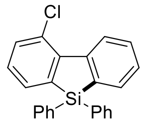
2p: 80%



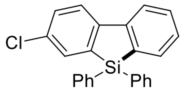
2q: 70%



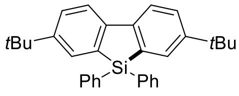
2r: 81%



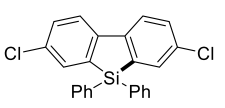
2s: 73%



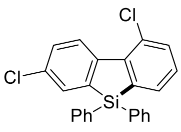
2t: 80%



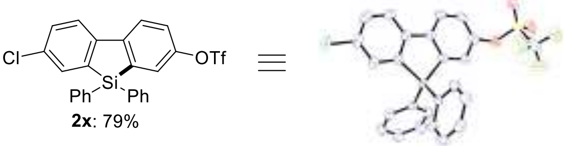
2u: 81%



2v: 73%



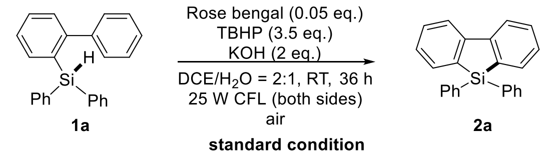
2w: 67%



2x: 79%

[a] Reaction conditions: **1** (0.2 mmol), rose bengal (0.05 eq.), TBHP (3.5 eq.), KOH (2 eq.), DCE/H_2O = 2:1 (v:v, 3 mL), irradiated with 2 x 25 W CFL (both sides) for 36 h under air and room temperature.

Table 4. Control experiments and radical scavenger experiments[a]



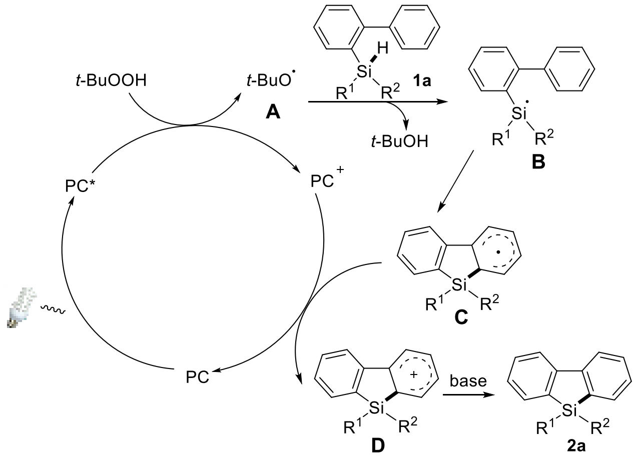
a) condition control experiments	
1: standard conditon	**2a**(77%)
2: no light	**2a**(0)
3: no Rose bengal	**2a**(trace)
4: no TBHP	**2a**(0)
5: no KOH	**2a**(0)+**3a**-silanol(92%)

b) radical inhibition study	
1: standard conditon	**2a**(**77%**)
2: add TEMPO(2 eq.)	**2a**(52%)
3: add TEMPO(3 eq.)	**2a**(35%)
4: add TEMPO(4 eq.)	**2a**(36%)
5: add BHT(2 eq.)	**2a**(0%)

[a] TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl. BHT = 2,6-di-tert-butyl-4-methylphenol.

The effect of substituents on aryl ring B or both rings was also investigated (Table 3). Overall, the position and electronic property of the function groups on aryl ring B has negligible influence on the reaction profile. Dibenzosiloles **2p**, **2r** and **2t** were obtained in good yields, which are similar to the results of **2i**, **2d** and **2h** in Table 2. For substrates with electron-donating methoxyl and electron-withdrawing chloro substituents, **2q** and **2s** were formed in comparable yields. Inspired by Oestreich's work, di-substituted precursors were also applied to our conditions, di-*tert*-butyl substituted dibenzosilole **2u** and dichloro substituted dibenzosiloles (**2v**, **2w**) could be obtained in moderate to good yields. Moreover, orthogonally difunctionalized silole monomer **2x**, which can undergo site-selective cross-coupling reactions, could be efficiently obtained in 79% yield in one step under the standard conditions. The crystal structure of **2x** was shown in the table.[21] The results in Table 2 and 3 demonstrated the excellent functional group compatibility of this mild visible-light photoredox-catalyzed radical silylation reaction to access a variety of benzannulated silole building blocks.

A series of experiments were then carried out to gain insights into the mechanism. When **1a** was irradiated under the standard conditions in the absence of TBHP or KOH, no desired product was observed (Table 4a). It is worth noting that without KOH, the reaction gave silanol in 92% yield. The reaction stopped completely without light irradiation, however, trace amount of **2a** could be observed in the absence of the photocatalyst. In addition, when different amounts of TEMPO were added to the reaction conditions, the reaction was suppressed gradually (Table 4b). The reaction was inhibited completely with butylated hydroxytoluene (BHT). The light/dark experiment was then conducted, where the reaction didn’t take place in the dark and can be switched on by turning on the light (see the Supporting Information, Figure S1). Moreover, with blue light (450 nm) irradiation, the quantum yield of this reaction was determined to be 0.28% (see the Supporting Information). These results ruled out the possibility of a chain reaction process but supported the photocatalytic pathway where oxidation of intermediate **C** is enabled by the photocatalyst instead of TBHP (Scheme 2).



Scheme 2. Proposed catalytic cycle of C-H silylation *via* visible-light photoredox catalysis. FG = functional group. PC = photocatalyst, rose bengal.

On the basis of the above results and previous literature,[22] a plausible reaction mechanism *via* a photocatalytic free-radical-type process is depicted in Scheme 2. The sequence would be initiated through visible light sensitization of rose bengal to its excited state rose bengal*, which reacts with *tert*-butyl hydroperoxide to produce *tert*-butoxyl radical (**A**). Abstraction of hydrogen from biarylhydrosilane (**1a**) would thus generate the corresponding silyl radical (**B**) and *t*-BuOH. Intramolecular radical addition delivers the radical intermediate **C**, which upon oxidation with the rose bengal$^+$ gives the carbocation intermediate **D**. Finally, species **D** is deprotonated, regenerating the aromatic system and affording the desired dibenzosilole **2a**.

In summary, we have developed an efficient and visible light-driven rose bengal-catalyzed radical silylation of biarylhydrosilanes, providing a mild and economic approach to the preparation of dibenzosiloles. A variety of substituted dibenzosiloles can be obtained in good yields with a cheap catalyst at room temperature under water/air compatible reaction conditions. Further application and development of this visible-light photoredox-catalyzed C-H silylation method and investigation of the detailed reaction mechanism are underway in our laboratory.

Experimental Section

Rose bengal (10.1 mg, 0.05 eq), KOH (24 mg, 2 eq.), and a solution of TBHP (5-6 M in decane, 0.14 mL, 3.5 eq.) were added to a solution of biaryl-2-yldiphenylsilane **1** (0.2 mmol) in the mixture solvent of DCE/H_2O = 3 mL (2:1). After sealing the tube, the mixture was stirred at room temperature and irradiated with 2 x 25 W CFL (both sides) for 36 h under air and room temperature. After the reaction finished, the reaction mixture was poured into 10 mL water and extracted with DCM (3 × 20 mL), the combined organic phase was dried over Na_2SO_4. The reaction mixture was concentrated under vacuum and purified by column chromatography to afford the desired product.

Acknowledgements

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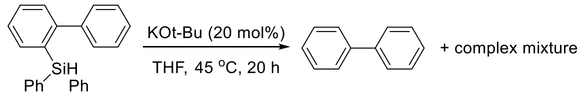
conducted under Grubbs' conditions, no desired product was observed (for details, see the Supporting Information).



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[21] CCDC-1574999 (**2x**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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COMMUNICATION

Visible-Light Induced Radical Silylation to Dibenzosiloles via Dehydrogenative Cyclization

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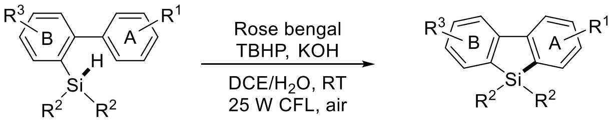

- cheap organic dye as the photoredox catalyst
- mild and water compatible conditions
- triflate group compatible conditions
- orthogonally difunctionalized silole can be obtained directly
- wide substrate scope, 24 examples, up to 86 % yield