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Report

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Oxidative Dehydrogenative Silylation-Alkenation Reaction of Alkyl Aromatics with Silanes

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Summary of main observation and conclusion A $Cu(OAc)_2$/DDQ/DTBP/Py system catalyzed oxidative dehydrogenative silylation-alkenation tandem reaction of readily available alkyl aromatic compounds with silanes was established. A variety of functionalized alkenyl organosilicon compounds were provided in good to high yields with a total β-(E) selectivity. The control experiments revealed that the transformation might proceed through a radical pathway.

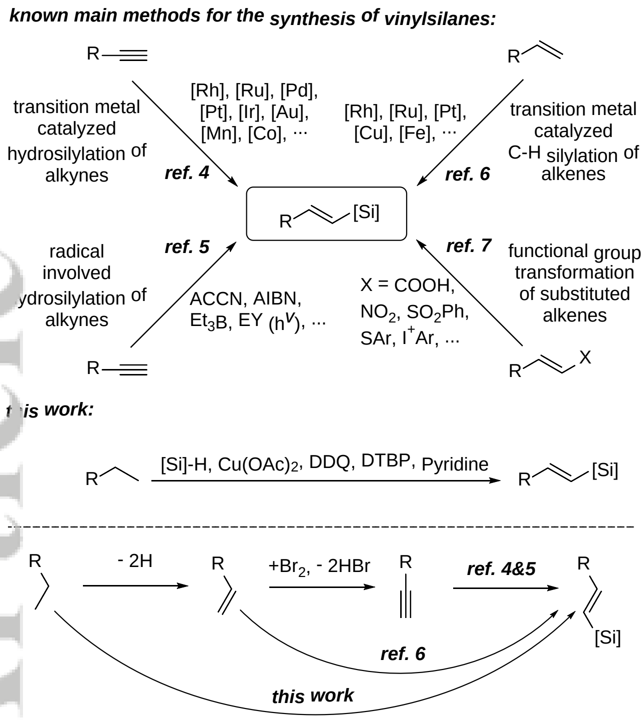
Background and Originality Content

Organosilicon compounds have been used as versatile building blocks in the preparation of organic molecules and functional materials.[1] Among them, alkenylsilanes are an important class of organosilicon compounds, which are particularly valuable intermediates in synthetic organic chemistry.[2] They are compatible with kinds of organic transformations and they are usually low toxic and easy to handle.[3] Because of the structural importance of this motif, its synthetic methods have been studied widely (Scheme 1). Among all the synthetic routes to the alkenylsilanes, transition metal catalyzed hydrosilylation of alkynes has become the most developed route in the past half century. A variety of transition metal catalysts have been successfully applied for the related transformations including Rh, Pt, Ru, Pd, Au, Ir, Mn and *et al.*[4] The radical based C−Si bond construction reactions of alkynes with silanes is also an important class of reactions for the preparation of vinylsilanes, started since even earlier times.[5] On the other hand, compared to these alkynes started methods, several oxidative C−H silylation of alkenes have been reported recently using transition metal catalysts such as Rh, Pt, Ru, Pd, Cu, Fe and *et al.*[6] In addition, a few functional group transformations of substituted alkenes have been reported to generate alkenylsilanes very recently. For examples, α,β-unsaturated carboxylic acid, β-nitroalkenes, vinyliodonium salts, alkenyl sulfones, and alkenyl sulfides have been used as available substrates for this protocol.[7]

Silyl-substituted styrene derivatives are extremely useful intermediates in modern organic chemistry, which are usually delivered by above mentioned methods from phenylacetylenes or styrenes.[4-7] Phenylacetylene is generally produced from styrene through bromination and the following twice dehydrobromination.[8] Styrene is a very important compound in chemical industry.[9] Direct dehydrogenation of ethylbenzene (EB) to styrene accounts for 85% of commercial production. EB is a frequently used reagent in the chemical industry and incredibly cheap organic solvent in chemistry lab. It is one of the most widely manufactured alkyl aromatic compounds in the world and is readily available from biorenewable sources.[10]

As the upstream material of phenylacetylene and styrene, EB is much cheaper and easier to get than phenylacetylene and styrene. Therefore, efficient construction of complex silyl-substituted styrenes by simple reactions using readily available EB derivatives is of apparent significance. Therefore, we report herein a new and efficient methodology for the highly stereo- and regio-selective oxidative dehydrogenative silylation-alkenation tandem reaction of alkyl aromatic compounds with silanes using the $Cu(OAc)_2$/DDQ/DTBP/Py catalyst system (Scheme 1).

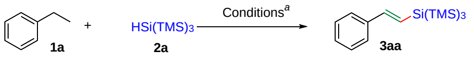
Scheme 1. Synthesis methods of vinylsilanes



Results and Discussion

Tris-(trimethylsilyl)silane [(Me$_3$Si)SiH, TTMSS] has been used in many radical involved transformations. It's commercially available and environmentally compatible, which are also stable under oxidative conditions. As shown in Scheme 2, our primary investigation in this study focused on the reaction of EB (**1a**) with TTMSS (**2a**), in the presence of metal catalyst and chemical oxidants. Cu(OAc)$_2$ was found as the most effective catalyst which provided the vinylsilane product **3aa** in 37% isolated yield (Scheme 2, entry 1). The addition of organic or inorganic bases usually increased the efficiency of the reaction (Scheme 2, entries 2–5). To our delight, the yield increased markedly to 61% when the transformation was conducted with one equivalent of pyridine as additive (Scheme 2, entry 5). Rescreening of metal salts revealed that Cu(OAc)$_2$ was still the best choice (Scheme 2, entries 6–14). Notably, the use of CuCl gave the same results as CuCl$_2$, thus demonstrating that both Cu(II) and Cu(I) catalyst precursors were able to facilitate this transformation (Scheme 2, entries 6–7). It is possible that the conversion between Cu(II) and Cu(I) species might occur during this reaction process.[11] Increasing or decreasing the amount of Cu(OAc)$_2$ led to slightly lower yields (Scheme 2, entries 15–16). Next, we tested the influence of the oxidant system. DDQ/DTBP gave the best results (Scheme 2, entries 17–22). The effect of temperature was also investigated and 120 °C was found to be optimal (Scheme 2, entries 23–24). The efficiency of the reaction decreased under air or O$_2$ atmosphere (Scheme 2, entries 25–26). Control experiments revealed that copper salt and two oxidants were all crucial for this transformation (Scheme 2, entries 27–29). When 3 equiv of EB in toluene was used instead of EB as solvent, the desired product 3aa was obtained in 32% yield.

Scheme 2. Screening of Reaction Conditions[a]

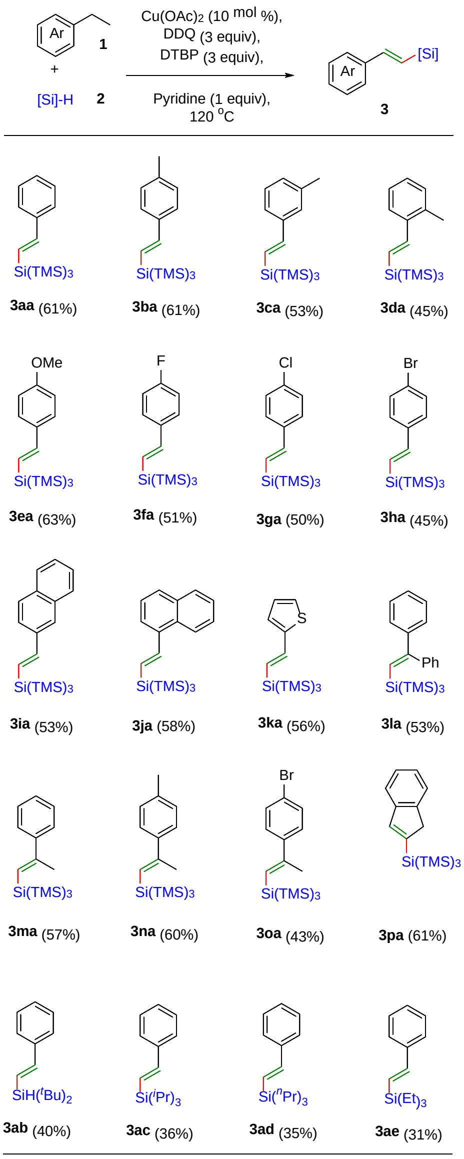


entry	catalyst	oxidant 1	oxidant 2	base	temp (^{o}C)	atmosphere	yield(%)[b,c]
1	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	--	120	Ar	37
2	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	DBU	120	Ar	37
3	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Et$_3$N	120	Ar	43
4	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	K$_2$CO$_3$	120	Ar	47
5	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	61
6	CuCl (10 mol %)	DDQ	DTBP	Py	120	Ar	45
7	CuCl$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	45
8	Cu(acac)$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	46
9	Cu(MeCN)$_4$PF$_6$ (10 mol %)	DDQ	DTBP	Py	120	Ar	36
10	FeCl$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	42
11	FeCl$_3$ (10 mol %)	DDQ	DTBP	Py	120	Ar	31
12	Fe(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	42
13	CoCl$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	43
14	NiCl$_2$ (10 mol %)	DDQ	DTBP	Py	120	Ar	31
15	Cu(OAc)$_2$ (5 mol %)	DDQ	DTBP	Py	120	Ar	33
16	Cu(OAc)$_2$ (15 mol %)	DDQ	DTBP	Py	120	Ar	58
17	Cu(OAc)$_2$ (10 mol %)	PBQ	DTBP	Py	120	Ar	0
18	Cu(OAc)$_2$ (10 mol %)	DTBP	DTBP	Py	120	Ar	0
19	Cu(OAc)$_2$ (10 mol %)	mCPBA	DTBP	Py	120	Ar	0
20	Cu(OAc)$_2$ (10 mol %)	DDQ	TBHP	Py	120	Ar	32
21	Cu(OAc)$_2$ (10 mol %)	DDQ	TBPB	Py	120	Ar	23
22	Cu(OAc)$_2$ (10 mol %)	DDQ	DDQ	Py	120	Ar	0
23	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	130	Ar	59
24	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	110	Ar	43
25	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	120	O$_2$	35
26	Cu(OAc)$_2$ (10 mol %)	DDQ	DTBP	Py	120	air	56
27		DDQ	DTBP	Py	120	Ar	0
28	Cu(OAc)$_2$ (10 mol %)		DTBP	Py	120	Ar	0
29	Cu(OAc)$_2$ (10 mol %)	DDQ		Py	120	Ar	0

[a] Reaction Conditions: **1a** (12 mmol), **2a** (0.2 mmol), oxidant 1 (0.6 mmol), oxidant 2 (0.6 mmol), base (0.2 mmol), 24 h. [b] Isolated Yields. [c] E/Z > 20:1.

Having found suitable conditions, the substrates scope of the copper-catalyzed oxidative dehydrogenative silylation-alkenation reaction of alkyl aromatic compounds with silanes was investigated as shown in Scheme 3. Firstly, the effect of different electron-donating and electron-withdrawing substituents in the *para* position of the aromatic ring of EB was investigated. Various functional groups were tolerated under the optimal conditions, affording the corresponding products **3ba** and **3ea**–**3ha** in good yields. 1-ethyl-4-nitrobenzene gave no desired product under the reaction conditions. Substituents in the *meta* and *ortho* position of the aromatic ring of EB were also tolerated, and the products **3ca** and **3da** were obtained in satisfactory yields. Next, other alkyl aromatic compounds lacking substituents on the aromatic ring (**1i**–**1l**), such as alkyl naphthalenes and diphenylethane, were all smoothly converted to the corresponding vinylsilane products (**3ia**–**3la**) in good to high yields. Heteroaryl such as ethyl thiophene also allowed the transformation to give the corresponding product **3ka** in 56% yield. Furthermore, isopropylbenzene (IPB, cumene), which is also one of the cheapest and most readily available organic solvents in chemistry lab, were converted to the corresponding vinylsilane products **3ma** in gratifying yield. Substituted IPBs **1n** and **1o** were also suitable substrates for this transformation. It is worth to mention that the condensed ring compound dihydro indene **1p** can react well with **2a** to deliver the corresponding product **3pa** in high yields. In addition, the scope of different silanes was evaluated and the expected products **3ab**–**3ae** were isolated in good to moderate yields. Propyl benzene gave no desired product under the reaction conditions.

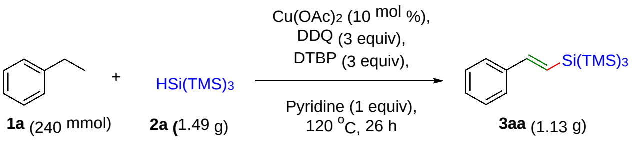
Scheme 3. Oxidative dehydrogenative silylation-alkenation reaction of alkyl aromatics with silanes[a,b]



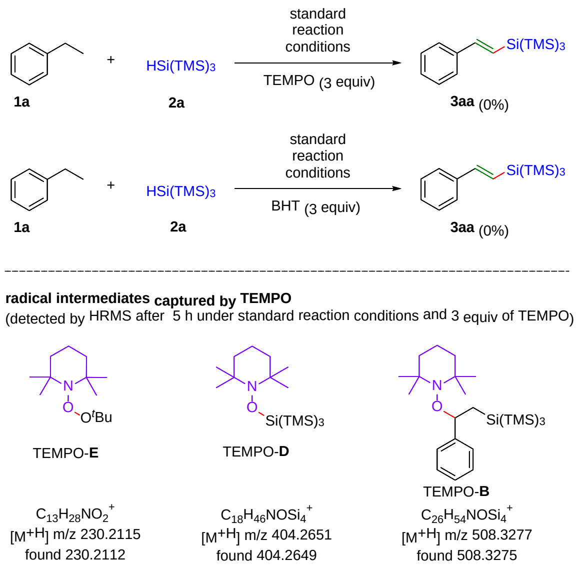
[a] Reaction Conditions: **1** (12 mmol), **2** (0.2 mmol), Cu(OAc)$_2$ (10 mol %), DDQ (0.6 mmol), DTBP (0.6 mmol), Pyridine (0.2 mmol), Ar, 24 h, 120 ºC. [b] Isolated Yields.

As shown in Scheme 4, we also explored this method on the gram scale level to show the consistency of this protocol. Under the standard reaction conditions, EB and TTMSS were taken as the starting materials and the product **3aa** was observed in 54 % yield.

Scheme 4. Scalability of the reaction to the multi-gram scale.

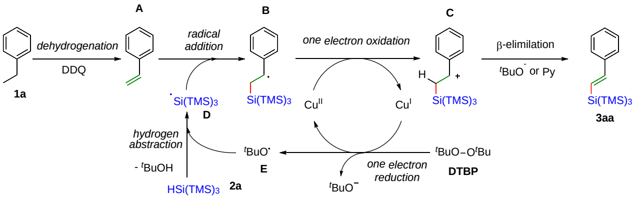


Scheme 5. Control Experiments



To probe the possible mechanism of this tandem silylation-alkenation reaction, some control experiments were carried out. Firstly, when 3.0 equiv of radical scavenger such as TEMPO or BHT was added to the reaction, no product **3aa** was obtained, which suggests the possibility of a radical pathway. And as shown in Scheme 2 (entries 25 & 26), the efficiency of the reaction decreased under air or O$_2$ atmosphere. These results also point to radical process. Next, we tried to confirm the formation of oxygen radical intermediate **E**, silicon radical intermediate **D** and carbon radical intermediate **B**. To this end, the template reaction between **1a** and **2a** was conducted under the standard reaction conditions and radical trapping agent TEMPO (3.0 equiv) was added after 5 hours (Scheme 5). To our delight, the TEMPO adducts TEMPO-**E**, TEMPO-**D**, and TEMPO-**B** could all be detected by HRMS in this test. The signal of styrene can be detected in this HRMS test too.

Scheme 6. Proposed mechanism



Based on above control experimental results and precedent literatures, a tentative reaction mechanism is proposed in Scheme 6. EB was first oxidized to generate styrene **A** in the presence of

DDQ. Then, the single electron transfer between DTBP and Cu(I) species occurs to generate *t*-butoxy radical **E,** which then abstracts a H atom from the starting silane **2a** and affords the Si radical **D**. Subsequently, the Si radical **D** adds to the double bond of **A** to give a radical adduct **B**. Radical intermediate **B** was then oxidized by Cu(II) species to deliver carbocation intermediate **C.** Finally, β-elimination of carbocation **C** was promoted by base (^{t}BuO$^-$ or pyridine) to give the product **3aa**.

Conclusions

In summary, we have developed a novel and practical tandem oxidative dehydrogenative silylation-alkenation reaction from easily available alkyl aromatic compounds and silanes for the efficient synthesis of silyl-substituted styrene derivatives by the use of a catalytic system combined by simple copper salt, oxidants and base. This transformation is highly efficient with the construction of one C−Si bond and removal of four H atoms. Further studies expanding the synthetic application of raw chemical materials such as alkyl aromatic compounds to high value-added intermediates are currently underway.

Experimental

To a 10 ml Schlenk tube with a magnetic stirring bar, Cu(OAc)$_2$ (.6 mg, 0.02 mmol, 10 mol%), and DDQ (136.2 mg, 0.6 mmol, 3 equiv) were added successively. Then the tube is evacuated briefly under high vacuum and charged with argon through using standard Schlenk techniques; this process is repeated three times. Then alkyl aromatics **1** (12 mmol, 60 equiv) was added. The resulting reaction mixture was performed at 120 ^{o}C for 4 hours. Silanes **2** (0.2 mmol), DTBP (110.5 μL, 0.6 mmol, 3 equiv) and Pyridine (16.1 μL, 0.2 mmol, 1 equiv) were added. The solution under argon was stirred at 120 ^{o}C for 20 hours. After the reaction was completed, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography to afford the desired compounds **3** (petroleum ether as the eluent).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2020xxxxx.

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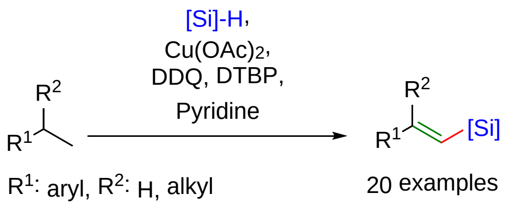

Oxidative dehydrogenative silylation-alkenation reaction of alkyl aromatics with silanes is described to produce silyl-substituted styrene derivatives.

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