Metal-Free Ammonium Iodide Catalyzed Oxidative Dehydrocoupling of Silanes with Alcohols

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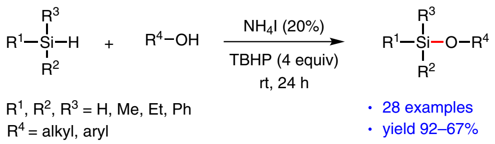

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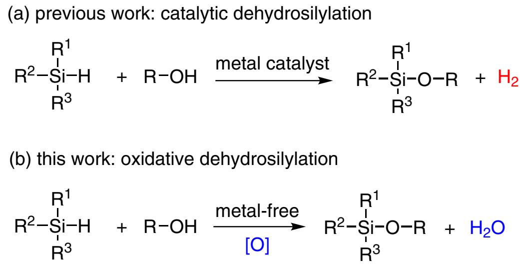
Abstract An ammonium iodide catalyzed direct oxidative coupling of silanes with alcohols to give various alkoxysilane derivatives was discovered. *tert*-Butyl hydroperoxide proved to be an efficient oxidant for this transformation. Attractive features of this protocol include its transition-metal-free nature and the mild reaction conditions.

Keywords silylation, ammonium iodide, silanes, alcohols, coupling, metal-free catalysis

Silyl ethers are useful moieties that have been widely used in the protection of hydroxy groups and in the production of silicon-based hybrid materials.[1] Generally, silyl ethers are prepared by the reaction of halosilanes with alcohols.[2] The catalytic dehydrogenative silylation of alcohols with a silane such as triphenylsilane or dimethyl(phenyl)silane as a silylating agent is an alternative approach for the preparation of silyl ethers that has attracted much attention. During the last decade, some elegant examples have been reported of catalytic dehydrogenative silylations in the presence of catalysts based on ruthenium,[3] rhenium,[4] iridium,[5] indium,[6] palladium,[7] copper,[8] boron,[9] N-heterocyclic carbenes,[10] alkali bases,[11] or others.[12] Mechanistic studies have shown that a highly active catalyst is generally necessary to convert the silane at a convenient rate. Although the only byproduct of the reaction is molecular hydrogen (Scheme 1, a), most of the reactions suffer from one or more disadvantages, such as the need for expensive catalysts, poor functional-group tolerance, low yields, or the need for rigorously anaerobic and water-free conditions.

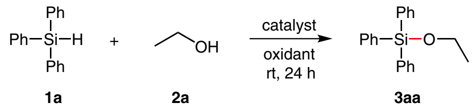


Scheme 1 Catalytic dehydrogenative silylation of alcohols by hydrosilanes

Oxidative cross-coupling has developed into a powerful strategy in recent years, and generally such reactions involve the direct coupling of two functional groups in the presence of a metal or nonmetal catalyst and an oxidant,[13] whereas the cross-coupling of silanes with other functional groups under oxidative conditions is less-well reported in the literature.[14] Recently, Liu and co-workers reported a decarboxylative silylation of unsaturated acids with silanes by a radical pathway.[14f] In continuation of our research efforts on the oxidative coupling reaction,[15] we report a dehydrogenative coupling of silanes with alcohols under oxidative conditions by using NH_4I as a catalyst and *tert*-butyl hydroperoxide (TBHP) as an oxidant (Scheme 1, b).

We began by optimizing the reaction by using triphenylsilane (1 mmol) and ethanol (1 mL) as reactants, NH_4I (0.10 mmol) as the catalyst, and 70 mass% aqueous TBHP (4.0 equiv) as the oxidant at room temperature (Table 1, entry 1). Experiments with various reaction conditions clearly demonstrated the generality of this reaction (entries 2–5). However, no product was observed in the absence of either the oxidant or the catalyst, clearly demonstrating the importance of both in the formation of product (entries 6 and 7). Other iodine sources KI, I_2, and tetrabutylammonium iodide (TBAI) gave 82, 75, and 69% yield, respectively (entries 8–10). With salts such as tetrabutylammonium bromide (TBAB) or tetrabutylammonium fluoride (TBAF), yields were lower than those obtained with iodide salts (entries 11 and 12). Screening of other oxidants such as hydrogen peroxide (H_2O_2), potassium persulfate ($K_2S_2O_8$), di-*tert*-butyl peroxide (DTBP), or benzoyl peroxide (BPO) under the same reaction conditions showed various results (entries 13–16). It was therefore confirmed that the best reaction conditions for this coupling reaction are those shown in Table 1, entry 3.

Table 1 Optimization of the Reaction Conditions[a]

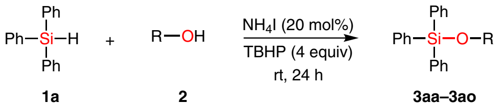


Entry	Oxidant (equiv)	Catalyst (mol%)	Yield[b] (%)
1	TBHP (4.0)	NH_4I (10)	79
2	TBHP (4.0)	NH_4I (5)	63
3	**TBHP (4.0)**	**NH_4I (20)**	**92**
4	TBHP (3.0)	NH_4I (20)	77
5	TBHP (2.0)	NH_4I (20)	58
6	–	NH_4I (20)	0
7	TBHP (4.0)	–	0
8	TBHP (4.0)	KI (20)	82
9	TBHP (4.0)	I_2 (20)	75
10	TBHP (4.0)	TBAI (20)	69
11	TBHP (4.0)	TBAB (20)	12
12	TBHP (4.0)	TBAF (20)	25
13	H_2O_2 (4.0)	NH_4I (20)	0
14	$K_2S_2O_8$ (4.0)	NH_4I (20)	52
15	DTBP (4.0)	NH_4I (20)	0
16	BPO (4.0)	NH_4I (20)	45

[a] Reaction conditions: Ph_3SiH (1 mmol), EtOH (1 mL), r.t., 24 h.
[b] Yield of the isolated product.

To explore the scope of the reaction, we next examined the reaction of triphenylsilane with various alcohols under the optimized reaction conditions (Table 2), and we obtained yields that varied from good to excellent. Generally, the reactions of Ph_3SiH with primary alcohols such as ethanol, methanol, propan-1-ol, butan-1-ol, isobutanol, or isoamyl alcohol resulted in excellent yields of up to 92% (entries 1–6), whereas secondary alcohols such as isopropanol, butan-2-ol, or cyclohexanol gave slightly lower yields of up to 77% (entries 7–9). Because of steric effects, no product was obtained in the case of a tertiary alcohol (entry 10). As a result of the oxidation of benzyl alcohol to the aldehyde by the present catalytic system, benzyl alcohol gave no yield in the reaction (entry 11). Long-chain systems and unsaturation in the alcohol had no effect on the yield of the product (entries 12 and 13). Good yields were obtained from the reactions of triphenylsilane with 2-phenylethanol or 2-(4-fluorophenyl)ethanol (entries 14 and 15).

Table 2 Oxidative Dehydrosilylation of Triphenylsilane with Various Alcohols[a]



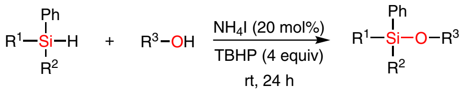
Entry	R	Product	Yield[b] (%)
1	Et	**3aa**	92
2	Me	**3ab**	85
3	Pr	**3ac**	91
4	Bu	**3ad**	89
5	*i*-Bu	**3ae**	82
6	isoamyl	**3af**	84
7	*i*-Pr	**3ag**	75
8	CH(Me)Et	**3ah**	77
9	Cy	**3ai**	72
10	*t*-Bu	**3aj**	–
11	Bn	**3ak**	–
12	$(CH_2)_7Me$	**3al**	86
13	$(CH_2)_2O_2CCH{=}CH_2$	**3am**	75
14	$(CH_2)_2Ph$	**3an**	85
15	$(CH_2)_2$-4-FC_6H_4	**3ao**	82

[a] Reaction conditions: Ph_3SiH (1 mmol), NH_4I (0.2 mmol), TBHP (4.0 mmol), ROH (1 mL), r.t., 24 h.
[b] Yield of the isolated product.

We next evaluated the scope of the reaction of various silanes with alcohols (Table 3). Compared with triphenylsilane, the reactions of methyl(diphenyl)silane, dimethyl(phenyl)silane, or triethylsilane with various alcohols gave slightly lower yields (Table 3, entries 1–8). These results clearly show that the yields of the product decreased with the decreasing aromaticity of the silane. Because of the less nucleophilic character of phenoxides, phenols gave lower yields under the optimal conditions, whereas good yields were obtained when the reaction was performed at 70 °C (entries 9–12). The reaction of diphenylsilane with phenylethanol or ethanol at 70 °C gave the corresponding dialkoxylated silane exclusively in moderate yield (entries 13 and 14).

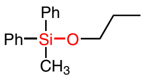
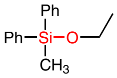
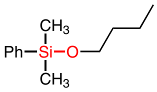
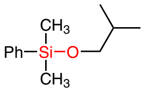
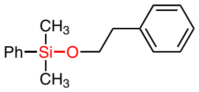
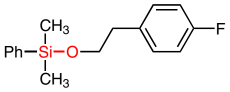
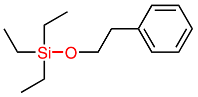
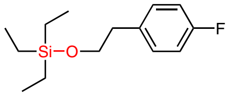
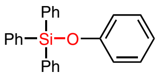
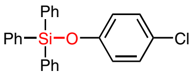
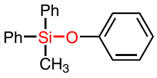
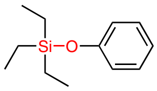
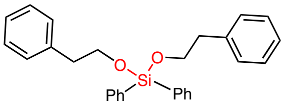
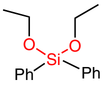
To examine the mechanism of this reaction, the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction mixture of triphenylsilane and ethanol under the optimized conditions. The alkoxysilane product **3aa** was isolated exclusively in 87% yield, indicating that free-radical intermediates are not involved in this transformation (Scheme 2, reaction 1). This product was obtained in 75% yield in presence of I_2 and TBHP (Table 1, entry 9), whereas no product was obtained in the absence of TBHP and the presence of I_2 (Scheme 2, reaction 2). Instead of the silylation product, $Ph_3SiOSiPh_3$ was obtained in 99% yield when an I_2/KOH catalytic system was used (Scheme 2, reaction 3). From these results, we surmised that hypoiodite, generated in situ, might be involved in the reaction. We confirmed this hypothesis by performing the reaction of triphenylsilane and ethanol in the presence of *tert*-butyl hypochlorite, which gave a 30% yield of the alkoxysilane product **3aa** (Scheme 2, reaction 4).

Table 3 Substrate Scope of the Oxidative Dehydrosilylation[a,b]



1 **2** **3ba–bo**

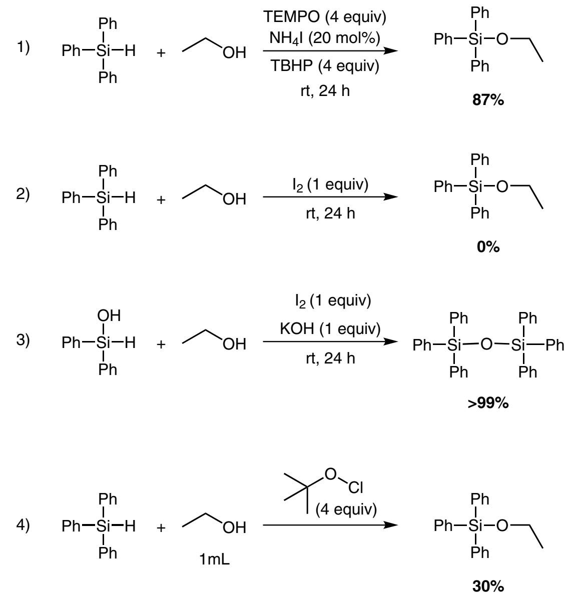
R^1, R^2 = H, Me, Et, Ph R^3 = alkyl, aryl

Entry		Product	Yield (%)
1	**3ba**		87
2	**3bb**		83
3	**3bc**		81
4	**3bd**		79
5	**3be**		75
6	**3bf**		73
7	**3bg**		67
8	**3bh**		62
9	**3bi**		86[c]
10	**3bj**		81[c]
11	**3bk**		79[c]
12	**3bl**		67[c]
13	**3bm**		74[c]
14	**3bn**		79[c]

[a] Reaction conditions: silane (1 mmol), NH_4I (0.2 mmol), TBHP (4.0 mmol), alcohol (1 mL), r.t., 24 h.

[b] Yields of the isolated products are reported.

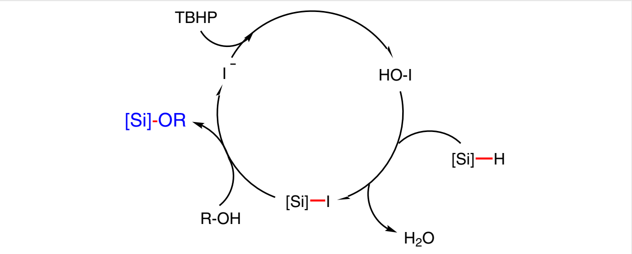
[c] Reaction performed at 80 °C.



Scheme 2 Results of control experiments

On the basis of above results and previous investigations by others,[16] we propose the mechanism shown in Scheme 3. Initially, combination of ammonium iodide with TBHP in situ generates a hypoiodite. This converts the silane into an iodosilane intermediate. Finally, the iodosilane intermediate reacts with the alcohol to give the silyl ether product, with regeneration of the iodide ion catalyst.

In summary, we have demonstrated a direct oxidative coupling reaction for the synthesis of alkoxysilanes from silanes and alcohols under mild conditions.[17] This efficient method provides a convenient approach for the synthesis of



Scheme 3 Proposed mechanism for the alkoxysilane synthesis

alkoxylated silane derivatives in the absence of any ligand, base, or metal. The method features readily available starting materials, an environmentally benign oxidant, and transition-metal-free characteristics. The extended scope of this reaction is under investigation, and the results will be discussed in due course.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588816.

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(17) **NH_4I-Catalyzed Oxidative Dehydrocoupling of Silanes with Alcohols: General Procedure**
70% aq TBHP (4.0 mmol) was added dropwise over 10 min to a solution of the appropriate silane (1.0 mmol) and NH_4I (0.20 mmol) in the appropriate alcohol (1 mL), and the mixture was stirred at r.t. until the reaction was complete (TLC). The reaction was then quenched with sat. aq $Na_2S_2O_3$, and the mixture was washed with brine, extracted with EtOAc, dried (Na_2SO_4), and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, PE).
Ethoxy(triphenyl)silane (3aa)
Colorless liquid; yield: 280 mg (92%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 6.4 Hz, 6 H), 7.42 (dt, *J* = 13.5, 6.6 Hz, 9 H), 3.90 (q, *J* = 7.0 Hz, 2 H), 1.26 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.49, 134.55, 130.06, 127.95, 59.85, 18.49. HRMS (TOF, EI$^+$): *m/z* calcd for $C_{20}H_{20}OSi$: 304.1283; found: 304.1285.