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Sodium Hydroxide Catalyzed Dehydrocoupling of Alcohols with Hydrosilanes

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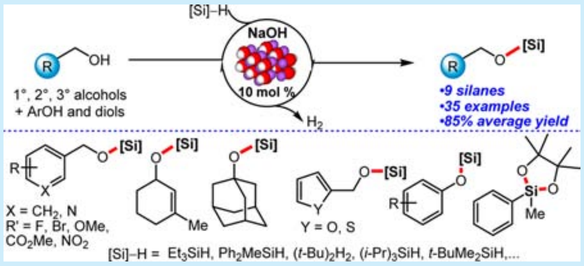
Supporting Information

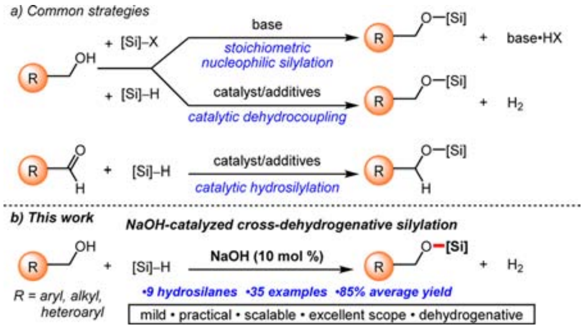
ABSTRACT: An O−Si bond construction protocol employing abundantly available and inexpensive NaOH as the catalyst is described. The method enables the cross-dehydrogenative coupling of an alcohol and hydrosilane to directly generate the corresponding silyl ether under mild conditions and without the production of stoichiometric salt byproducts. The scope of both coupling partners is excellent, positioning the method for use in complex molecule and materials science applications. A novel Si-based cross-coupling reagent is also reported.



Our group has explored direct C−H bond functionalization reactions[1] enabled by catalysts based on Earth-abundant alkali metals wherein neither coupling partner has been prefunctionalized.[2] Such dehydrogenative functionalization methods are valuable from the perspective of atom- and step-economy; however, they are intrinsically challenging.[3] We recently reported the direct C−H silylation of aromatic heterocycles with hydrosilanes catalyzed by potassium *tert*-butoxide (KO-*t*-Bu) alone.[4] We sought to investigate the alkali-metal catalysis concept for the construction of other silicon-containing bond classes. We were thus drawn to the O−Si bond due to its importance in protecting group chemistries,[5] its utility as a traceless directing group in organic synthesis,[6] and its prevalence in a number of important functional material classes.[7] Silyl ether functionalities have also been implicated in enhancing the pharmacokinetic properties of medicines.[8]

A large number of catalytic methods for the construction of O−Si bonds have been developed: the direct silylation of alcohols by transition-metal catalysis,[9] Brønsted and Lewis acids/bases,[10] and catalytic hydrosilylation of carbonyl compounds[11] have been the most commonly employed protocols (Scheme 1a). However, despite decades of work, the most straightforward method for the construction of the O−Si bond is the treatment of alcohols with moisture-sensitive chlorosilanes in the presence of nucleophilic catalysts and a base to scavenge the HCl generated.[12] Of course, this method may have limited utility for acid-sensitive substrates. Moreover, this classical method is unsuitable in certain especially challenging silylations such as the silylene protection of 1,2-diols, especially in the cases of hindered systems. In these cases, the use of specialized substrate/silane combinations and particularly reactive systems[13] or toxic electrophilic silicon reagents[14] is necessary. As a result, the development of an effective and convenient O−Si bond construction methodology which circumvents the production of stoichiometric salt byproducts and avoids the use of toxic and moisture-sensitive electrophilic silicon sources, while simultaneously improving the scope in comparison to previous methods, would be of interest and significant practical value to chemists working in a variety of fields.

Scheme 1. Strategies for the Synthesis of Silyl Ethers



During our prior studies of catalytic C−H silylation using Earth-abundant alkali metal bases, a robustness evaluation revealed that a compound containing an −OH group was adventitiously silylated under certain conditions.[4a] This was not entirely unanticipated since base-catalyzed methods for the formation of O−Si bonds by dehydrocoupling with hydrosilanes have been previously explored.[15] However, base-catalyzed systems reported thus far often use highly basic activators,[15a−c] tend to require the use of additives such as crown-ethers to obtain suitable reactivity,[15a,c,d] and can require unacceptably high temperatures (i.e., >150 °C).[10e] From a practical utility perspective, these reports have shown only moderate functional group tolerance with respect to both the alcohol and hydrosilane partner, rendering them generally unsuitable for complex

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molecule applications. Fluoride salts have also been shown to catalyze the dehydrocoupling; however, reactions can be energy intensive (i.e., temperatures between 0 and 180 °C), require highly polar solvents (e.g., NMP), and are also generally reported with modest substrate scope.[10b−e,15f] Nevertheless, an efficient base-catalyzed (and ideally fluoride-free) strategy would be attractive, potentially representing a convenient, low cost, and transition-metal-free strategy for dehydrogenative silyl ether synthesis.

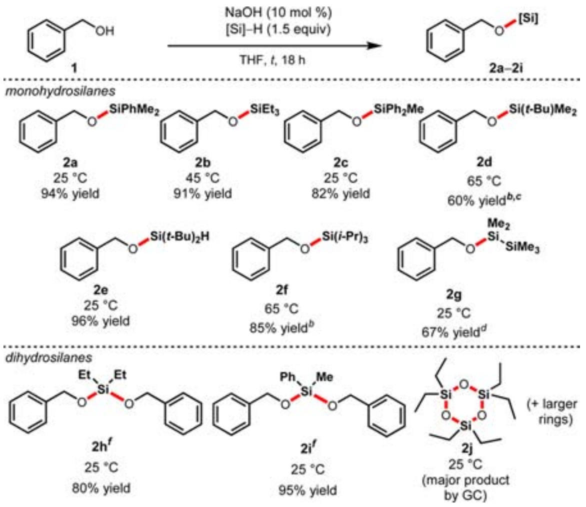
Conversely, the Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) has also been shown to be a catalyst for the dehydrogenative silylation of alcohols with hydrosilanes.[10a] This method proceeds under mild conditions and has a useful functional group tolerance. However, the presence of Lewis basic nitrogen functionalities dramatically lowers the reactivity or leads to complete catalyst deactivation. Moreover, cyclic ethers such as THF derivatives are ring-opened in the course of the reaction except in rare special cases. These issues and others limit the utility of Lewis acid catalyzed methods, especially in alkaloid natural product synthesis and the derivatization and manipulation of pharmaceutical targets.

We sought to develop a cross-dehydrogenative O−Si bond coupling reaction that employs a mild and inexpensive catalyst, operates under mild conditions in the absence of costly additives, and shows superior functional group tolerance to prior strategies. Thus, inspired by the work of others and encouraged by our previous results in silylation catalysis,[4] we herein report a practical and general cross-dehydrogenative O−Si bond construction methodology catalyzed by NaOH alone (Scheme 1b). The protocol has excellent functional group compatibility, proceeds well in the presence of Lewis basic moieties and sensitive functionalities on the substrate, satisfies sterically demanding as well as fragile hydrosilanes, and operates under mild conditions. The silyl ether products are formed in high yield, and H_2 is generated as the byproduct.

Unfunctionalized benzyl alcohol was chosen as the model substrate along with $PhMe_2SiH$ as the hydrosilane (Scheme 2). The reaction proceeded in THF as the solvent with 10 mol % NaOH as the catalyst to afford 94% yield of the desired benzyl silyl ether **2a** at ambient temperature. The reaction can be performed without regard for air and moisture with an identical 94% yield; however, siloxane $(PhMe_2Si)_2O$ is generated as a byproduct, likely arising from the double silylation of H_2O.

We next evaluated the scope of the hydrosilane and observed that a large scope of hydrosilanes were amenable to the NaOH-catalyzed reaction (Scheme 2). Monohydrosilanes with small- and medium-sized aryl (**2a** and **2c**) and alkyl (**2b**) substituents gave the corresponding silyl ethers in high yields. The much larger TBDMS and TIPS groups could also be introduced, yielding **2d** and **2f**, respectively; however, it was found that the use of DMF as a cosolvent was necessary to obtain good yields in these cases.[16] The use of the bulky dihydrosilane di-*tert*-butylsilane led to efficient monosilylation, generating **2e** in high yield; however, the use of less sterically hindered dihydrosilanes led exclusively to Si-tethered species **2h** and **2i** at ambient temperature. The method tolerates even fragile disilanes such as $H{-}Si_2(CH_3)_5$ leading to product **2g** and could thus be useful for applications to silicon materials.[17] Finally, the reaction of diethylsilane with water under NaOH catalysis results in the formation of cyclic siloxanes, with trisiloxane **2j** being the major product (by GC analysis).[18] With these data in hand, we proceeded to explore the alcohol scope, and a wide variety of hydroxyl-containing small molecules proved to be excellent substrates in this reaction (Table 1). The NaOH-catalyzed cross-dehydrogenative coupling is amenable to substrates containing aromatic (Table 1, entries 1−12, 21, and 22) as well as aliphatic (entries 13−20) moieties. The reaction proceeds well in the presence of arenes bearing halides (entries 2 and 3), nitro- (entry 4), ether (entry 6), and alkyl (entry 10) functionalities leading to the corresponding silyl ethers in generally high yields.

Scheme 2. NaOH-Catalyzed Dehydrogenative Si−H/O−H Cross Coupling: Scope of the Hydrosilane[a,e]

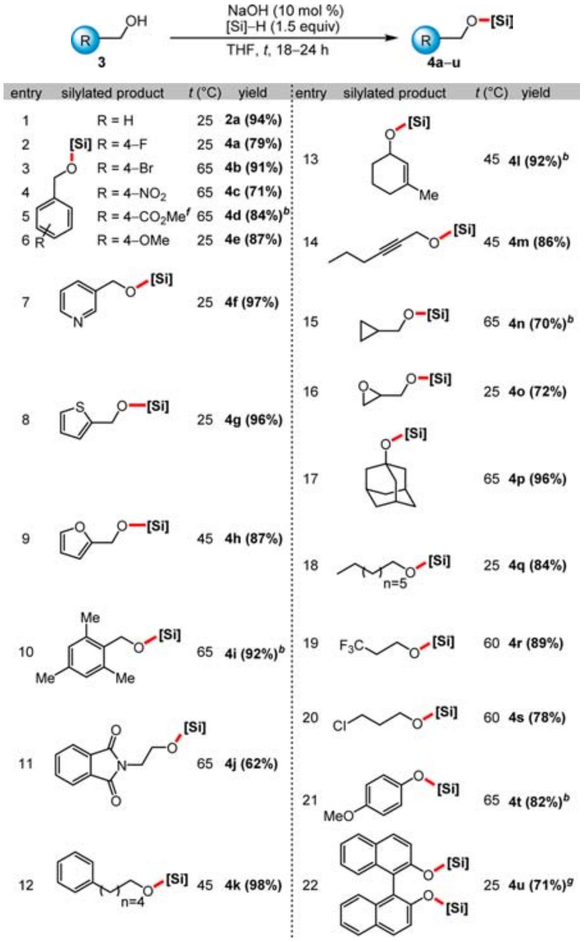


[a] Reactions performed with 0.5 mmol of starting material and 0.5 mL of THF at the prescribed temperature. [b] A 1:1 mixture of DMF/THF was used as the solvent. [c] 3.0 equiv of hydrosilane and 20 mol % NaOH. [d] The reaction was conducted for 24 h. [e] Yield of isolated material after purification. [f] Yield based on a theoretical maximum of 0.25 mmol of Si-tethered product.

Electron-rich aromatic heterocycles (entries 8 and 9) are likewise excellent substrates for the dehydrocoupling providing the corresponding silyl ethers in high yield. A 2° allylic alcohol (entry 13) and a 1° propargylic alcohol (entry 14) also react well, with no reduction or hydrosilylation detected. Cyclopropanes are also tolerated (entry 15). Functionalities that deactivate organic and organometallic Lewis acid catalysts such as pyridines (entry 7) and those that are acid-sensitive such as an epoxide (entry 16) are silylated in 97% and 72% yield, respectively. The 3° alcohol 1-adamantol (entry 17) also undergoes dehydrosilylation, affording the silyl ether product in excellent yield. We were surprised to find that functionalities such as an aromatic methyl ester (entry 5)[19] and a phthalimide (entry 11),[20] which are known to readily undergo hydrosilylation or direct reduction in the presence of mixtures comprising Lewis bases and hydrosilanes, react well under the reaction conditions with little (5−7%) hydrosilylation detected only in the latter case. Alkyl−CF_3 and alkyl−Cl moieties likewise react well (entries 19 and 20). ArOH fragments such as *p*-methoxyphenol and BINOL are silylated in good yields (entries 21 and 22).

A number of mechanistic pathways for Lewis base activation of silanes in the context of related dehydogenative couplings have been proposed.[12,21−23] Most recently, Oestreich and co-workers investigated the mechanism of a related dehydrogenative silyl ether synthesis using a KO-*t*-Bu-based system.[15c] In that insightful study, the authors propose the formation of a key pentacoordinate potassium silicate by interaction of KO-*t*-Bu with hydrosilane under similar conditions. An analogous activation mode is likely also occurring in our reported system. It is interesting to note that

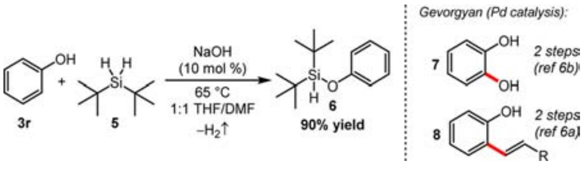
Table 1. Scope of the Alcohol Partner[a,d,e]



entry	silylated product	t (°C)	yield
1	R = H	25	**2a** (94%)
2	R = 4–F	25	**4a** (79%)
3	R = 4–Br	65	**4b** (91%)
4	R = 4–NO_2	65	**4c** (71%)
5	R = 4–CO_2Me[f]	65	**4d** (84%)[b]
6	R = 4–OMe	25	**4e** (87%)
7		25	**4f** (97%)
8		25	**4g** (96%)
9		45	**4h** (87%)
10		65	**4i** (92%)[b]
11		65	**4j** (62%)
12		45	**4k** (98%)
13		45	**4l** (92%)[b]
14		45	**4m** (86%)
15		65	**4n** (70%)[b]
16		25	**4o** (72%)
17		65	**4p** (96%)
18		25	**4q** (84%)
19		60	**4r** (89%)
20		60	**4s** (78%)
21		65	**4t** (82%)[b]
22		25	**4u** (71%)[g]

[a]Reactions performed with 0.5 mmol of starting material and 0.5 mL of THF at the prescribed temperature. [b]2:3 DMF/THF used as the solvent. [c]3.0 equiv of hydrosilane, 20 mol % of NaOH, DME (1.0 M) solvent. [d][Si] = $PhMe_2SiH$. [e]Yield of isolated material after purification. [f]Base-catalyzed transesterification occurs to a minor extent. See the Supporting Information. [g]1,2-Dimethoxyethane is used as the solvent; 3 equiv of $PhMe_2SiH$.

Scheme 3. Applications to Directing Group Chemistry[a,b]



[a]Reaction performed with 0.5 mmol of starting material and 0.5 mL of THF. [b]Yield of isolated material after purification.

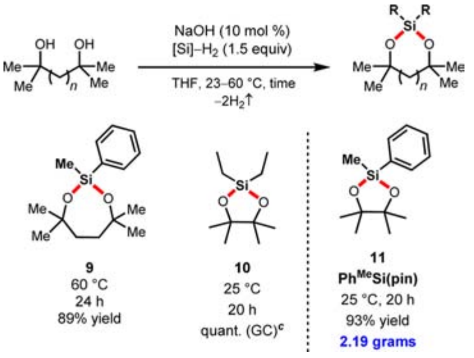
NaOH is a much weaker base than KO-*t*-Bu so the exact nature of the interaction will require further study. This may explain the successful silylation of more sensitive examples such as **4s** under our conditions.

With a scope of substrates established, we turned to employ our NaOH-catalyzed method to the synthesis of silyl ethers that could be used in directing group chemistry and cross-coupling reactions. For example, the reaction of phenol (**3r**) with the bulky and commercially available di-*tert*-butylsilane **5** with 10 mol % of NaOH furnishes the corresponding di-*tert*-buylhydrosilyl ether **6** in high yield and without undesirable double activation of the Si−H bond (Scheme 3). Gevorgyan has reported that silane **6** is elaborated by palladium-catalyzed C−H functionalization reactions such as *ortho*-oxidation to generate catechols (Scheme 3, **6** → **7**)[6b] and *ortho*-alkenylation to access α-hydroxy styrenes (**6** → **8**) via the corresponding silanol.[6a]

Cognizant of the importance of heteroatom-substituted arylsilanes in C−C and C−X bond-forming reactions,[12,21b,24] we sought to employ the catalytic O−Si bond construction method for the expedient and cost-efficient synthesis of novel cross-coupling reagents.[24] We aimed to construct the silicon analogue of the aryl boronic acid pinacol ester PhB(pin), $PhSi^{Me}$(pin), where Me is chosen as a nontransferrable group, and evaluate its suitability as an aryl-transfer reagent. This would be beneficial given the increased abundance and lower cost of silicon relative to boron[24,25] and the potential for improved stability or overall utility of the silicon reagent.[24,26] However, one-step preparation of $PhSi^{Me}$(pin) would involve a silylene protection of a 1,2-diol, which has proven challenging, especially in the case of sterically hindered diols such as pinacol even using standard electrophilic silicon sources (i.e., [Si]−Cl).[13,14,15d,27,28] This is normally due to either poor cyclizat-ion reactivity, uncontrollable oligomerization, or rearrangements.[13,14,15d] As a result, and to the best of our knowledge, this cyclic siloxane compound has only been prepared by refluxing pinacol in THF for 24 h with (a) the dichlorosilane in the presence of stoichiometric pyridine (a yield was not reported)[27] or (b) the dihydrosilane in the presence of a catalytic quantity of Cp_2TiCl_2/*n*-BuLi, providing the product in 67% isolated yield.[28]

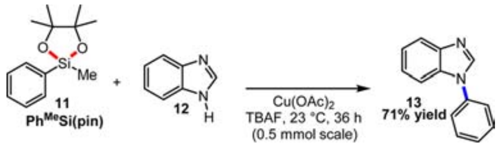
Fortunately, it was found that the NaOH-catalyzed dehydrosilylation is an excellent strategy for the synthesis of cyclic siloxanes. The method was successful in providing access to silicon-protected diols with varying ring sizes and functionalities at silicon from the corresponding diols and hydrosilanes enabling the high-yielding preparation of **9** and **10**. It was noticed, however, that **10** was hydrolytically unstable and could not be isolated. Finally, reacting the commercially available $PhMeSiH_2$ with pinacol resulted, upon addition of the NaOH catalyst, in the immediate and vigorous evolution of hydrogen. The reaction is complete in 20 h at ambient temperature, giving a high yield (2.19 g, 93% yield) of the corresponding colorless liquid $PhSi^{Me}$(pin) **11** (Scheme 4) after purification by distillation. Note that since the silylation protocol described in this paper produces stoichiometric H_2, the reaction, especially when performed on a

Scheme 4. Silylene Protection of Diols and Synthesis of $PhSi^{Me}$(pin)[a,b]



[a]Reactions performed on a 1.0 mmol scale, except for the synthesis of **11**, which is performed on a 10 mmol scale. [b]Yields are of isolated material after purification. [c]Quantitative conversion by GC, but product cannot be isolated.

Scheme 5. Application of $\mathrm{PhSi^{Me}(pin)}$ to Aryl Transfer[a,b]



[a] Cu-mediated reaction performed on a 0.5 mmol scale. [b] Yields are of isolated material after purification.

reasonable scale as in the case of **11**, should be conducted in a well-vented system and under conditions that are appropriately suitable and safe (see the Supporting Information for more details). As with **9** and **10**, no oligomers, polymers, or uncyclized products were detected. With this compound in hand, its ability to transfer the phenyl moiety bound to silicon in a Hiyama-type cross-coupling reaction could for the first time be investigated.[24,29] To test this, the $\mathrm{PhSi^{Me}(pin)}$ reagent was treated with benzimidazole **12**, $Cu(OAc)_2$, and TBAF, and the mixture was stirred at ambient temperature for 36 h to provide the desired *N*-arylation product **13** in 71% yield (Scheme 5).[30]

In summary, we have developed a mild and general cross-dehydrogenative O−Si bond construction protocol using NaOH as the catalyst. The reaction is robust, scalable, shows exceptional scope, and even enables the silylene protection of challenging diols. The convenience and breadth of the chemistry should make this method accessible to chemists and nonchemists alike for the synthesis of silyl ethers in a myriad of contexts and across a wide variety of fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01687.

Full experimental details and characterization of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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