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Selective Synthesis of Silacycles by Borane-Catalyzed Domino Hydrosilylation of Proximal Unsaturated Bonds: Tunable Approach to 1,n-Diols

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Abstract. Tris(pentafluorophenyl)boron-catalyzed domino hydrosilylation of substrates carrying unsaturated functionalities in proximal arrangement is presented to produce silacycles. Excellent levels of efficiency and selectivity were achieved in the cyclization by the deliberate choice of the hydrosilane reagents. The key to successful cyclic hydrosilylation is the reactivity enhancement of the second intramolecular hydrosilylation by proximity effect. Not only dienes but also enones, enynes, ynones and enimines readily afford medium-sized silacycles under convenient and mild conditions. The cyclization proceeds with acceptable diastereoselectivity mainly controlled by the conformational bias towards inducing additional stereogenic centers. The silacycles obtained from this reaction were converted to 1,n-diols or 1,n-amino alcohols upon oxidation, thus rendering the present cyclization a powerful tool for accessing synthetically valuable building blocks.

Keywords: silacycles, domino reaction, amino alcohols, $B(C_6F_5)_3$ catalyst, hydrosilylation

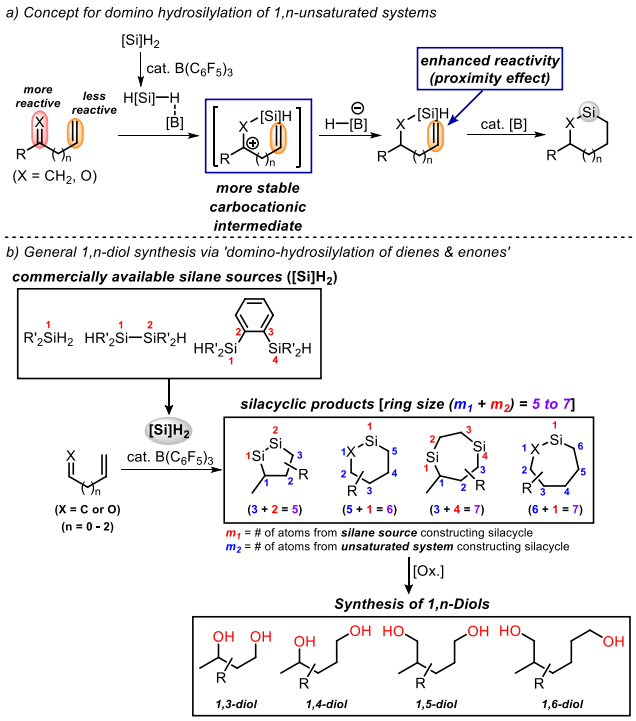
Introduction

Hydroxyl groups are ubiquitous in natural products, synthetic intermediates, pharmaceuticals, and bio-materials.[1] In particular, diols are a prominently featured class of scaffolds in synthesis owing to the large number of versatile transformations that they allow.[2] As a result, the development of synthetic protocols for the synthesis of 1,n-diols, especially from abundant unsaturated bonds, has been extensively studied.[3-5] A variety of 1,2- and 1,3-diols can be synthesized mostly by the 1,2-dihydroxylation of olefins[3] and the reduction of β-hydroxy carbonyl compounds,[4] respectively. While approaches to access 1,4-diols have been rarely explored, recently, a few elegant examples for the synthesis of 1,4-diols have been reported.[5] Despite these extensive efforts, a *general and widely applicable synthetic method for accessing a range of 1,n-diols* is elusive thus far. One traditional strategy to access 1,n-diols is a boracycle synthesis via tandem hydroboration of dienes and subsequent oxidation.[6] However, only a single borylating reagent, the unstable thexylborane, has been shown to mediate the cyclic hydroboration, thus limiting the synthetic applicability of this strategy.[7]

These considerations led us to envision another approach leading to 1,n-diols based on a silacycle formation via hydrosilylation and subsequent oxidation.[8,9]In fact, procedures for the preparation of silacyclic compounds via metal-catalyzed intramolecular hydrosilylation of olefinic substrates were reported several decades ago.[10] However, these procedures suffer from narrow scope in either substrates and silane reactants. In this context, we wondered whether the $[B(C_6F_5)_3]$, a Lewis acidic borane catalyst that has been widely utilized recently to facilitate hydrosilylation of various unsaturated systems via an unique η^1-activation mode of Si–H bonds in hydrosilane reagents, [11,12] can mediate the desired 'domino hydrosilylation' of proximal unsaturated bonds such as dienes and enones with dihydrosilanes to form the corrseponding silacycles (Scheme 1a). It was anticipated that the initial *intermolecular* hydrosilylation will occur at the more reactive unsaturated bonds where more stable carbocation intermediates[13] can be generated to afford monohydrosilyl species. This intermediate may undergo a subsequent *intramolecular* hydrosilylation at the neighboring unsaturated bonds, leading to the corresponding silacyclic products. It was predicted that the proximity effect and the fact that no translational entropy penalties have to be paid by turning the *inter*molecular into an *intra*molecular reaction may facilitate this cyclic hydrosilylation towards the less reactive unsaturated bonds that

otherwise do not react under normal borane-catalyzed hydrosilylation conditions.[14]

Described herein is a general methodology to form medium-sized silacycles ($m + n$ = 5~7) by a borane-catalyzed domino hydrosilylation of proximal unsaturated bonds (m = 3~6) with dihydrosilanes (n = 1~4, Scheme 1b). The silylating reagents (n) were finely tuned to react with proximal unsaturated bonds while varying the hydrocarbon chain linker (m) between two unsaturated bonds. As envisioned, subsequent oxidation of silacycles was facile under the established oxidative conditions to furnish the corresponding 1,n-diols.

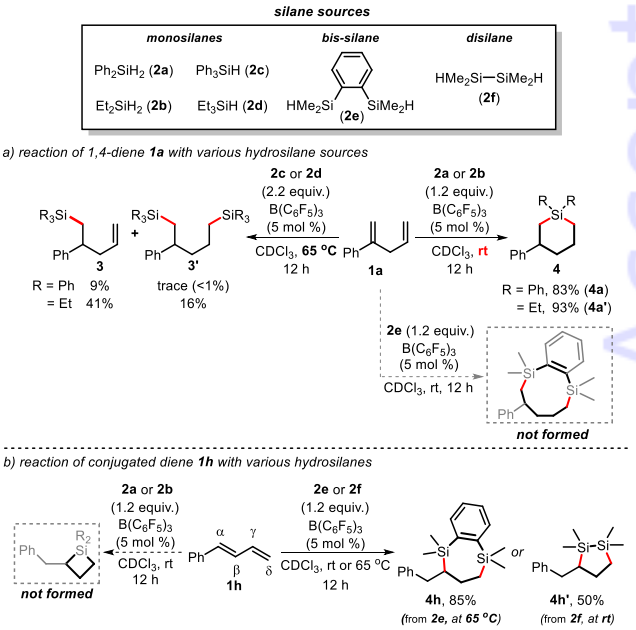


Scheme 1. Synthesis of 1,n-diols via [$B(C_6F_5)_3$]-catalyzed domino hydrosilylation

Results and Discussion

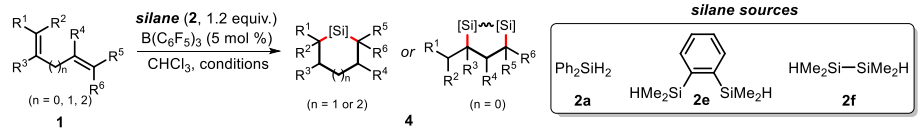
Domino Hydrosilylation of Dienes. To test our working hypothesis on the tunable reactivity towards the silacycle formation, we commenced our studies on the $B(C_6F_5)_3$-catalyzed hydrosilylation of 1,4-diene **1a** with various types of silanes (Scheme 2a). Diene **1a** bearing a phenyl group at the 2-position was deliberately chosen as a model substrate since two double bonds were predicted to display a distinct reactivity towards the borane-mediated hydrosilylation, in which the reaction course was assumed to be guided by the relative stability of emerging carbocationic intermediates.[13] We envisaged that a phenyl-substituted double bond will react first with the borane-silane adduct[12d] and then terminal olefin will be engaged by a subsequent intramolecular hydrosilylation. Indeed, a reaction of **1a** with Ph_3SiH (**2c**, 2.2 equiv.) in the presence of $B(C_6F_5)_3$ catalyst (5 mol %) took place almost exclusively at the styrenyl position, albeit in poor efficiency. The use of an analogous monohydrosilane, Et_3SiH (**2d**, 2.2 equiv.), resulted in a similar selectivity pattern, but with higher reactivity when compared to Ph_3SiH (Scheme 2a, left). The terminal olefin of **1a** was sluggish toward hydrosilylation even at high reaction temperature (65 °C).

However, diphenylsilane Ph_2SiH_2 (**2a**, 1.2 equiv.) was reacted smoothly with diene **1a** at room temperature to afford a 6-membered silacycle (**4a**) in good yield. Interestingly, diethylsilane Et_2SiH_2 (**2b**) was also facile to form the corresponding silacycle (**4a'**) in excellent yield (Scheme 2a, right). These results clearly support our initial hypothesis that intrinsically low reacting unsaturated bonds can greatly enhance their reactivity by altering its reaction mode from inter- to intramolecular. The efficiency in the formation of silacycles was changed depending on the ring size.[10a] For instance, when diene **1a** was treated with a bis-silane **2e**, the desired 9-membered silacycle was not formed (Scheme 2a, bottom). This tunable reactivity in the silacycle formation was also seen with other types of dienes. Indeed, 1,3-conjugated diene **1h** was readily reacted with bis-silane **2e** to form a 7-membered disilacycle (**4h**) in high yield (Scheme 2b). The resultant connectivity in this cyclization is notable in that β- and δ-carbon centers relative to the phenyl group in **1h** are connected to two silicon atoms of **2e**. Likewise, disilane **2f** was reacted with *trans*-1-phenyl-1,3-butadiene (**1h**) to furnish a 5-membered ring (**4h'**) albeit in moderate yield. On the other hand, monosilanes **2a** or **2b** did not undergo the desired cyclization to generate 4-membered silacycles. Again, these results address the importance of optimizing reactivity in the silacycle formation by tuning the types of silanes.



Scheme 2. Borane-catalyzed domino hydrosilylation of 1,3- and 1,4-dienes with hydrosilanes

Table 1. Scope of domino hydrosilylation of dienes[a]



diene	silane (2)	product
1a	2a	4a[b], 83%
1b	2a	4b, 77% d.r. = 84:16
1c	2a	4c, 91% d.r. = 87:13
1d	2a	4d[c], 74% d.r. = 82:18
1e	2a	4e[b,c], 59% d.r. = 52:48
1f	2a	4f, 85% d.r. = 90:10
1g	2a	4g, 78% d.r. = 55:45
1h	2e	4h[c], 85%
1h	2f	4h'[b], 50%
1i	2e	4i[c], 52%
1j	2f	4j, 53%
1k	2e	4k[c], 38%

[a] Conditions: **1** (0.5 mmol), **2** (0.6 mmol) and [$B(C_6F_5)_3$] (5 mol %) in $CHCl_3$ (0.5 mL) at room temperature for 24 h under argon atmosphere. [b] Reaction was conducted for 12 h. [c] Reaction at 65 °C

To test the generality of the present domino hydrosilylation route to silacycles, the scope of dienes was first investigated (Table 1). 2-Phenyl-1,4-pentadiene (**1a**) smoothly underwent the domino hydrosilylation with diphenylsilane Ph_2SiH_2 (**2a**, 1.2 equiv.) at room temperature in the presence of 5 mol % of $B(C_6F_5)_3$ catalyst in chloroform solvent (see Supporting Information for the optimization studies). A 6-membered silacycle product (**4a**) was obtained in good yield. A same molecular skeleton of 1,4-diene having two substituents at the 2- and 4-position (**1b**) was facile for the silacycle formation (**4b**). Interestingly, the cyclization was occurred with high diastereoselectivity favoring a *trans*-product over *cis*-isomer (84:16). The structure of **4b** was determined by X-ray crystallographic analysis (Figure 1, left). A reaction of diphenylsilane with a 1,4-diene bearing one endocyclic olefin (**1c**) gave a bicyclic silacycle (**4c**) in 91% yield with high diastereoselectivity (87:13) to furnish an additional stereocenters at the newly generated bicyclic junction. A different type of silabicyclic compound (**4d**) was obtained at slightly higher temperature from 1,4-diene bearing one *exo*-methylene double bond (**1d**) that was derived from a natural product, isopulegol. In this cyclization, a high level of diastereoselectivity (82:18) was induced. 1,5-Diene substituted at the 2- and 5-position (**1e**) underwent the domino hydrosilylation with moderate efficiency to afford a 7-membered silacycle (**4e**). In contrast to the 6-membered cases (**4b-4d**), a similar mixture of two diastereomers (52:48) was observed. Structure of a *trans*-isomer of **4e** was confirmed by an X-ray crystallographic analysis (Figure 1, right). Notably, the diastereoselectivity was significantly increased when 1,5-diene has one internal double bond bearing substituents at the 2- and 6-position (**1f**), wherein a 6-membered silacycle (**4f**) was produced with high diastereoselectivity (90:10). A bicyclic silyl product **4g** was obtained from (+)-limonene (**1g**), a 1,5-diene bearing one methylene and one cyclic double bond, in reaction with diphenylsilane (1.2 equiv.) at room temperature with 5 mol % of $B(C_6F_5)_3$ catalyst. While three stereogenic centers were newly generated in this cyclization, a mixture of two diastereomers were observed.

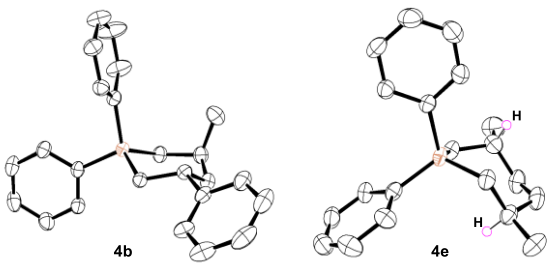


Figure 1. Crystal structure of **4b and 4e**

As the next type of diolefinic substrates, we turned our attention to *conjugated* dienes to test the feasibility of the silacycle formation. Domino

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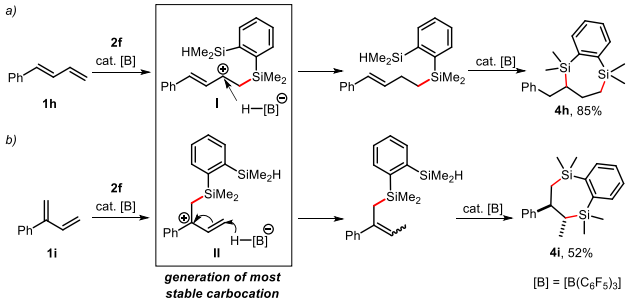
hydrosilylation of 1,3-dienes was envisioned to be interesting in that its cyclization regioselectivity may be changed depending on the type of substituents. Indeed, 1-phenylbutadiene **1h** was reacted with 1,2-bissilylbenzene **2e** or disilane **2f** to afford the corresponding 7- and 5-membered disilacycle **4h** and **4h'**, respectively. This cyclization outcome to form C–Si bonds at the C-2 and C-4 position can be understood by assuming that the reaction proceeds via the most stable carbocationic intermediates (Scheme 3a).

It is noteworthy that a reaction of 2-phenylbutadiene (**1i**) with **2e** gave rise to a disilacycle product **4i** where two C–Si bonds formed at the C-1 and C-3 position (Scheme 3b). Interestingly, this cyclization afforded a single *trans*-isomeric product, which was unambiguously determined by NMR analysis. Preliminary mechanistic studies suggest that while the hydrosilylation of 1-phenylbutadiene **1h** takes place first at the terminal double bond via an allylic carbocation intermediate **I**, reaction of 2-phenylbutadiene **1i** proceeds in a 1,4-hydrosilylation manner via an allyl benzyl cationic intermediate **II** (see Supporting Information for details). Additional types of conjugated dienes also underwent the reaction to form the corresponding silacycles. For instance, a 5-membered silacycle **4j** was obtained in a reaction of 1,1,4,4-tetrasubstituted-1,3-diene **1j** with disilane **2f** presumably via an analogous mechanistic pathway as that of **1h**. In addition, 2,3-dimethylbutadiene **1k** was cyclized by domino hydrosilylation with bissilylbenzene **2e** to afford a 7-membered silacycle **4k**, as similar to that of **1i**. It needs to be mentioned that transition metal-catalyzed diboration, as an alternative route to diols, can afford only 1,2- or 1,4-diols from 1,3-dienes.[15] Therefore, the present borane-catalyzed domino hydrosilylation of conjugated dienes offers a valuable complementary approach for the regioselective synthesis of 1,3-diols upon the subsequent oxidation.



Scheme 3. Proposed reaction pathways of 1- or 2-substituted conjugated dienes

Domino Hydrosilylation of Enones. We next turned our attention to an additional type of substrates: enones (Table 2). Since the desired 1,2-oxasilinane products were predicted to be easily oxidized to afford 1,n-diols,[9] the success in this domino hydrosilylation of enones could further widen the substrate scope and synthetic value of the current approach. Moreover, the resulting oxasilinanes obtainable from enones eventually furnish one-carbon shortened diols upon oxidation when compared to the silacycles derived from analogous 1,n-diene substrates. Since ketones are known to exhibit generally higher reactivity towards the $B(C_6F_5)_3$-catalyzed hydrosilylation than olefinic double bonds,[11h,k] we hypothesized that the initial hydrosilylation to enones will occur at the carbonyl double bond. In addition, the pioneering study of Dussault and co-workers demonstrated that an alkoxysilane, a putative intermediate in the present domino hydrosilylation of enones (see the figure in Table 2), can undergo the intramolecular hydrosilylation smoothly to form the corresponding silacyclic product.[16] Based on these considerations, we predicted that the desired domino hydrosilylation of enones would be facile. As a proof of concept, 3-methyl-1-phenylbut-3-en-1-one (**6a**) was readily reacted with diphenylsilane (**2a**, 1.2 equiv.) at 0 °C by the action of $B(C_6F_5)_3$ catalyst (5 mol %) to deliver 3,5-disubstituted 1,2-oxasilinane (Table 2, **7a**). More pleasingly, the reaction was highly diastereoselective favoring *anti*-isomer (*d.r.* >99:1), confirmed by X-ray crystallographic analysis (Figure 2).

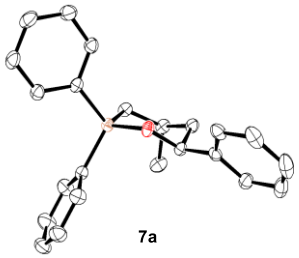


Figure 2. Crystal structure of **7a**

Likewise, derivatives of β,γ-unsaturated enones (**6b**,**6c**) were highly facile for the cyclic hydrosilylation with exclusive formation of the corresponding *anti*-silacycles. In addition to β,γ-unsaturated enones, γ,δ-unsaturated enone **6d** also underwent the domino hydrosilylation with diphenylsilane to afford a 7-membered oxasilepane product **7d**. Interestingly, as observed above in the cyclization of dienes, diastereoselectivity in the formation of this 7-membered silacycle (**7d**) was not notable (56:44). However, it was greatly increased (*d.r.* >99:1) in the formation of a 6-membered silacycle (**7e**) from the same type of γ,δ-unsaturated enone **6e** bearing an *internal* double bond. In addition, this reaction could be performed on a 5 mmol scale to afford the desired silacyclic product **7e** in 78% (1.21 g) yield, demonstrating the synthetic utility of the current procedure (see the Supporting Information for detailed procedure). A dienone (**6f**) also underwent a regioselective domino hydrosilylation to afford **7f**. As anticipated, a more distant double bond at the δ,ε-position relative to the carbonyl group was observed to be kinetically less favorable than β,γ-olefinic double bond. In fact, no 7-membered silacycle was

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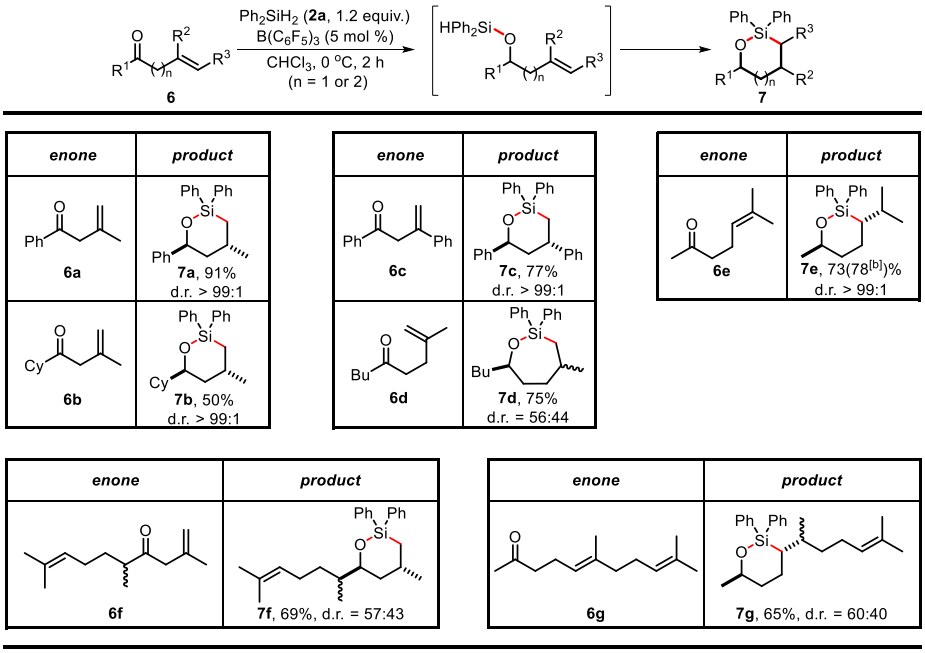
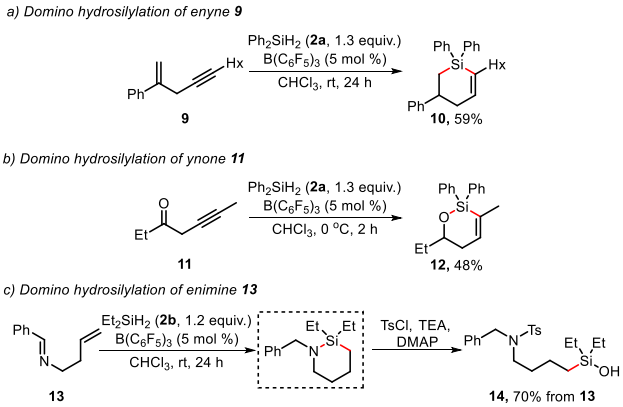
Table 2. Scope of domino hydrosilylation of enones[a]



[a] Conditions: **6** (0.3 mmol), **2a** (0.36 mmol) and [$B(C_6F_5)_3$] (5 mol %) in $CHCl_3$ (0.5 mL) at 0 °C for 2 h under argon atmosphere. [b] Reaction was performed on a 5 mmol scale.

formed in this reaction. In reaction of dieneone **6g**, the γ,δ-double bond relative to the carbonyl group reacted selectively with diphenylsilane to furnish an oxasilinane product **7g** via 6-exo cyclization. These results indicate that the regioselective domino hydrosilylation can be efficiently achieved by tuning the ring size of resultant silacyclic products, thus highlighting the potential utility of the present method to more complex enone substrates.

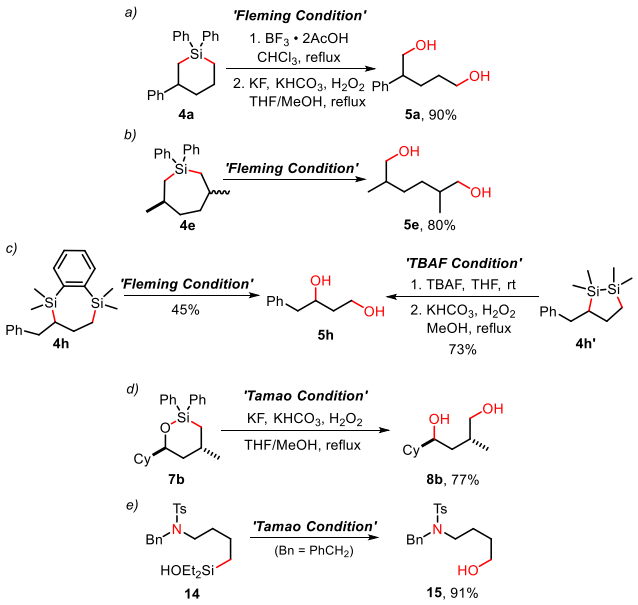


Scheme 4. Extension of the present procedure: Domino hydrosilylation of other unsaturated systems

Domino Hydrosilylation of Other Unsaturated Systems. Besides dienes and enones, we were pleased to see that the current domino hydrosilylation strategy could be successfully applied to additional types of unsaturated systems (Scheme 4). 1,4-Enyne (**9**) was smoothly reacted with diphenylsilane using the $B(C_6F_5)_3$ catalyst (5 mol %) at room temperature to afford a 6-membered cyclic vinylsilane **10** via an *endo-dig* cyclization process (Scheme 4a).[10g] When an ynone (**11**) was subjected to the present hydrosilylation protocol, unstable 6-membered silacyclic product **12** was obtained in moderate yield (Scheme 4b).[10h] These preliminary results foresee the potential utility of our strategy for the formation of sp^2 C–Si bonds that can readily be transformed by subsequent cross-coupling reactions, which were extensively studied by Denmark and Hiyama.[17] Moreover, we observed that γ,δ-olefinic imine **13** participated in the present hydrosilylation with diethylsilane. Although we could not isolate the desired azasilacycle mainly owing to the unstable nature of N–Si bond, we indeed obtained the corresponding aminosilane product **14** upon *in situ* hydrolysis and subsequent N-tosylation for the ease of isolation (Scheme 4c).

Application: Oxidation of Silacycles. Importantly, as we anticipated at the beginning of this study, silacyclic products obtained by the present domino hydrosilylation procedure were efficiently converted to the corresponding 1,n-diols and amino alcohols under the Fleming-Tamao oxidation conditions (Scheme 5).[9] When silinane (**4a**) or silepane (**4e**) were subjected to the Fleming protocol, the corresponding 1,5-diol (**5a**) and 1,6-diol (**5e**) were obtained in good yields, respectively (Scheme 5a and 5b). In addition, 1,3-diol (**5h**) was obtained from the oxidation of either a disilyl-containing 7-membered silacycle (**4h**) or a 5-membered silacycle having a bis-silyl moiety (**4h'**) in synthetically acceptable yields (Scheme 5c). Tamao oxidation of oxasilinane

(**7b**) and aminosilane (**14**) was also facile to afford the corresponding 1,4-diol (**8b**) and 1,4-amino alcohol (**15**), respectively (Scheme 5d and 5e).



Scheme 5. Conversion of silacycles to the corresponding diols via oxidation

Conclusion

In summary, we have shown that a borane-catalyzed domino hydrosilylation of readily available compounds having proximal unsaturated bonds with various dihydrosilanes furnishs silacycles. Substrate scope was broad to include remote dienes, conjugated dienes, enones, enimines, enynes, and ynones. While the selectivity of the initial intermolecular hydrosilylation is governed by the relative stability of *in situ* generated carbocation intermediates, the subsequent intramolecular hydrosilylation takes place at the remaining less reactive unsaturated bonds that are otherwise unreactive under the borane catalysis. Another attractive feature of this approach lies in the availability of a broad range of dihydrosilanes altering their reactivity and ring size leading to silacycles of variable sizes. Thus, the reaction efficiency in the domino hydrosilylation can be tuned effectively by the choice of flexible dihydrosilanes as well as by the design of proximal unsaturated bonds of substrates. The obtained silacycles were readily oxidized to the corresponding 1,n-diols or 1,n-amino alcohols as versatile synthons. Investigations on further synthetic utility of silacycles that become readily accessible through this study are now in progress to include a direct cross-coupling of C–Si bonds with organic electrophiles.

Experimental Section[18]

General Procedure for $B(C_6F_5)_3$-Catalyzed Domino Hydrosilylation of Dienes

To a solution of $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol, 5 mol %) in $CHCl_3$ (0.5 mL) in a screw capped reaction vial was added dihydrosilane (**2**, 0.60 mmol, 1.2 equiv.) under argon atmosphere. Diene (**1**, 0.50 mmol, 1.0 equiv.) was then added and the reaction mixture was allowed to heat at the indicated temperature and time. The reaction mixture was cooled down to room temperature, concentrated under reduced pressure and purified by column chromatography on silica gel with *n*-hexane/EtOAc to give the desired silacyclic products **4a-4k**. Products **4b**, **4c**, **4d**, **4f** and **4g** were further purified by preparative HPLC using Shim-pack PREP-ODS (H) kit or YMC-pack SIL column to obtain the major/minor diastereomers.

General Procedure for $B(C_6F_5)_3$-Catalyzed Domino Hydrosilylation of Enones

To a solution of $B(C_6F_5)_3$ (7.7 mg, 0.015 mmol, 5 mol %) in $CHCl_3$ (0.4 mL) in a screw capped reaction vial was added diphenylsilane (**2a**, 66.8 µL, 0.36 mmol, 1.2 equiv.) under argon atmosphere. The reaction mixture was allowed to cool down to 0 °C. Ketone substrate (**6**, 0.30 mmol, 1.0 equiv.) was subsequently added under argon atmosphere and allowed to stir for 2 h at 0 °C. After 2 h, all volatiles were removed under reduced pressure and the crude product was purified by flash column chromatography with *n*-hexane/EtOAc to give the desired silacyclic products. Products **7d**, **7f** and **7g** were further purified by preparative HPLC using Shim-pack PREP-ODS (H) kit or YMC-pack SIL column to obtain the major/minor diastereomers.

Acknowledgements

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[18] All experimental details are available in the Supporting Information. CCDC 1552310 (**4b**), CCDC

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1469939 (**4e**) and CCDC 1468851 (**7a**) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.com.ac.uk/data_request/cif.

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FULL PAPER

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