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Silylium-Ion-Promoted Ring-Opening Hydrosilylation and Disilylation of Unactivated Cyclopropanes

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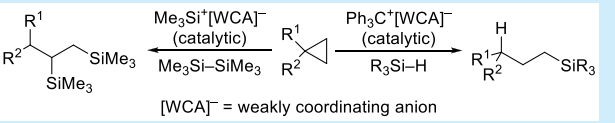
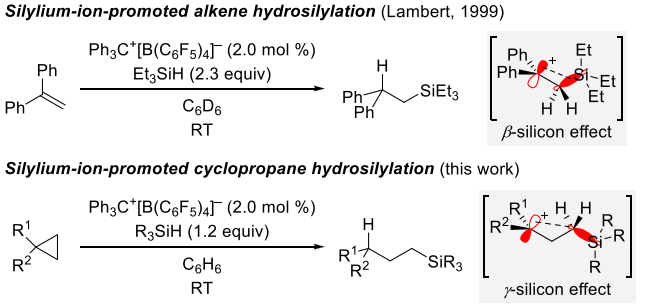
ABSTRACT: A silylium-ion-promoted ring-opening hydrosilylation of unactivated cyclopropanes is reported. The reaction is facilitated by the γ-silicon effect, and the regioselectivity is influenced by various stabilizing effects on the carbenium-ion intermediates, including the β-silicon effect. The experimental observations are in accord with the computed reaction mechanism. The work also showcases the ability of silylium ions to isomerize cyclopropyl to allyl groups, and the resulting α-olefins engage in a silylium-ion-mediated disilylation with hexamethyldisilane.



Synthetic methodology involving silylium ions and, more precisely, silylium-ion-like species as catalysts or reactants is an emerging area.[1,2] After the controversy over their isolation and characterization had been settled,[3] these reactive intermediates were successfully employed in various types of reactions in which silylium ions are consumed but regenerated from appropriate precursors.[4,5] This was termed self-regeneration of silylium-ion catalysts,[4b] and one such example is the silylium-ion-mediated hydrosilylation of alkenes (Scheme 1, top).[4a] The key intermediate in this reaction is a carbenium ion that is stabilized by the β-silicon effect[6] (gray box). The catalytic cycle is initiated by silylium-ion formation with the Corey reaction[7] and subsequently maintained by the related hydride abstraction with the aforementioned carbenium ion from the hydrosilane reagent.

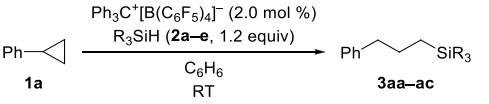
Scheme 1. Silylium-Ion-Promoted Hydrosilylation of Alkenes and Cyclopropanes



An open question is whether another stabilizing effect exerted by Si–C(sp^3) σ-bonds could be exploited for the silylium-ion-mediated hydrosilylation of unactivated cyclopropanes (Scheme 1, bottom). The so-called γ-silicon effect lends stabilization to carbenium ions by percaudal participation of the back lobe of the Si–C(sp^3) σ-bond (gray box).[8−10] Literature evidence indeed supports the feasibility of the anticipated transformation.[11−14] Nagahara and co-workers had achieved the hydrosilylation of these cyclopropanes with $ClMe_2SiH$ (1.0 equiv) and $AlCl_3$ (20 mol %).[11] More recently, a BBr_3-mediated cyclopropane hydroboration with $PhSiH_3$ as the hydride source was also accomplished.[12] $B(C_6F_5)_3$ alone[13a] or as part of a frustrated Lewis pair[13b] was shown to open or isomerize the three-membered ring, respectively.[15] In this Letter, the hydrosilylation and, on the basis of recent work from our laboratory,[16] the disilylation of unactivated cyclopropanes promoted by silylium ions are reported.

We began our investigation by reacting cyclopropylbenzene (**1a**) with different hydrosilanes **2** (Table 1). The starting silylium ion was generated by the addition of 2 mol %

Table 1. Variation of the Hydrosilane[a]



entry	hydrosilane	time (min)	yield (%)[b]
1	Et_3SiH (**2a**)	15	84
2	$^iPr_3SiH$ (**2b**)	10	93
3	$^tBuMe_2SiH$ (**2c**)	150	43[c]
4	Ph_3SiH (**2d**)	180	no conversion[d]
5	Me_2PhSiH (**2e**)	60	–[c,e]

[a]All reactions were performed on a 1.0 mmol scale. [b]Isolated yield after purification by flash chromatography on silica gel. [c]Full conversion of the cyclopropane. [d]Substituent scrambling at the silicon atom was faster than ring opening. [e]Several hydrosilylation products were detected as a result of substituent scrambling.

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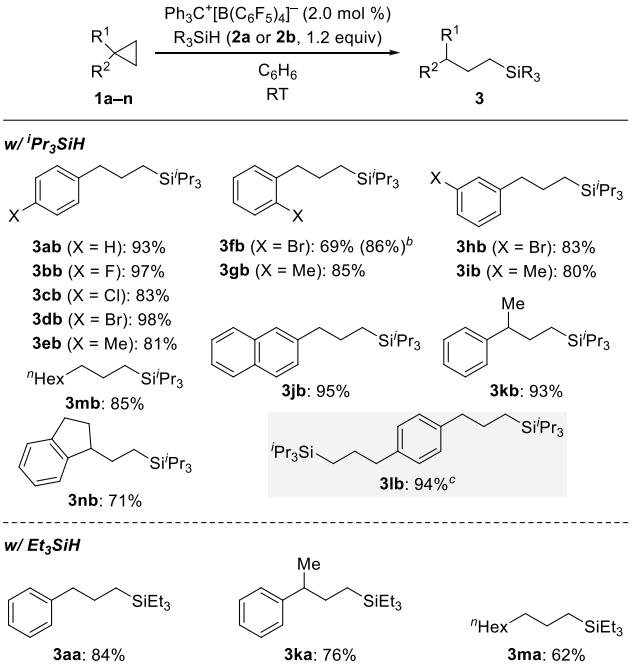
$Ph_3C^+[B(C_6F_5)_4]^-$ to 1.2 equiv of the indicated hydrosilane; the cyclopropane was then slowly added. For Et_3SiH (**2a**), the vigorous reaction was finished within a few minutes, and the desired ring-opened product **3aa** was isolated in 84% yield after flash chromatography on silica gel (entry 1). $^iPr_3SiH$ (**2b**) reacted equally fast in a better yield (**1a** → **3ab**, entry 2); however, bulkier $^tBuMe_2SiH$ (**2c**) required a longer reaction time, and the yield was moderate (**1a** → **3ac**, entry 3). Other hydrosilanes such as Ph_3SiH (**2d**) and Me_2PhSiH (**2e**) did not participate in the ring opening but underwent facile substituent scrambling at the silicon atom (entries 4 and 5).[17]

The scope of the cyclopropane hydrosilylation was examined with $^iPr_3SiH$ (**2b**) as the hydrosilane (Scheme 2, top). High

Scheme 2. Scope of the Ring-Opening Hydrosilylation of Mono- and 1,1-Disubstituted Cyclopropanes[a]

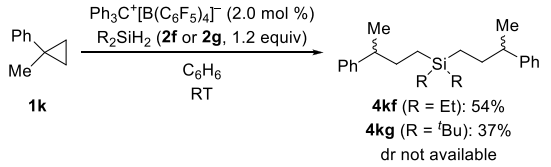


[a]Unless otherwise noted, isolated yields after purification by flash chromatography on silica gel. [b]Yield determined by ^1H NMR spectroscopy with CH_2Br_2 as an internal standard. [c]2.2 equiv of $^iPr_3SiH$ (**2b**).

yields were obtained throughout for various electronically modified cyclopropylbenzenes (**1a–i** → **3ab–ib**); the functional-group tolerance was typical for a reaction involving highly electrophilic silicon intermediates, and carbonyl groups were not compatible. A *β*-naphthyl group (**1j** → **3jb**) and geminal disubstitution (**1k** → **3kb**) were also tolerated. A *p*-phenylene derivative decorated with two cyclopropyl groups reacted equally well (**1l** → **3lb**, gray box). Yields were lower for alkyl-substituted cyclopropanes but still synthetically useful (**1m,n** → **3mb,nb**). Representative substrates were also shown to react with Et_3SiH (**2a**), and the lower yields were in line with our expectations (Scheme 2, bottom).

The reactions of 1,1-disubstituted cyclopropane **1k** with dihydrosilanes Et_2SiH_2 (**2f**) and $^tBu_2SiH_2$ (**2g**) were also tested (Scheme 3). Both ring-opening hydrosilylations worked in acceptable yields but for different reasons. Substituent scrambling[17] competes with the ring opening in the case of Et_2SiH_2 (**2f**), and steric hindrance hampers the formation of

Scheme 3. Ring-Opening Hydrosilylation with Dihydrosilanes[a,b]

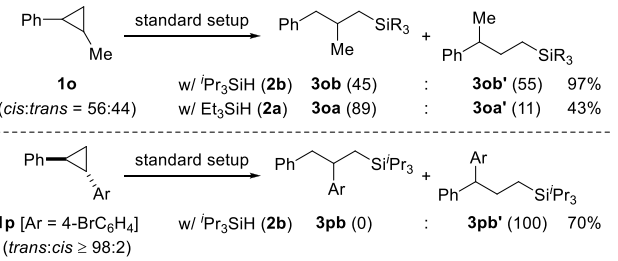


[a]Isolated yields after purification by flash chromatography on silica gel. [b]No diastereomers were detected by GLC analysis.

the fully alkylated silane with $^tBu_2SiH_2$ (**2g**) (cf. Table 1, entry 3). The crude ^1H NMR spectra were too complex to extract any valuable information about the diastereomeric ratio of **4kf** and **4kg**, and we were even unable to separate the diastereomers by GLC analysis, probably because of their low polarity.

The situation changed with 1,2-disubstituted cyclopropanes such as **1o** and **1p** because the proximal and distal C–C bonds (relative to the phenyl substituent) are less differentiated (Scheme 4). With $^iPr_3SiH$ (**2b**), regioisomer **3ob′** was formed

Scheme 4. Ring-Opening Hydrosilylation of 1,2-Disubstituted Cyclopropanes[a,b]



[a]Isolated yields after purification by flash chromatography on silica gel. [b]Ratios of regioisomers determined by ^1H NMR spectroscopy of the crude reaction mixture.

along with **3ob** in an almost equimolar ratio whereas the rearrangement was less prevalent with Et_3SiH (**2a**) as the hydrosilane (top). Moreover, **1p** afforded rearranged product **3pb′** exclusively with **2b** (bottom); the same transformation with **2a** was messy (not shown). These findings establish the occurrence of Wagner–Meerwein shifts and illustrate the delicate balance between carbenium-ion-stabilizing effects.

Deuterium-labeling experiments were performed to shed further light on the reaction mechanism (Scheme 5). When cyclopropylbenzene (**1a**) was reacted with $^iPr_3SiD$ (**2b**-d_1) as well as Et_3SiD (**2a**-d_1), deuterium incorporation was detected in both the benzylic and homobenzylic positions of **3ab**-d_1 and **3aa**-d_1, respectively (top). A [1,2] hydride shift explains the intermediacy of the corresponding carbenium ions. In a similar way, deuteration revealed that the hydrosilylation of the 1,2-disubstituted cyclopropane **1p** goes through one or two [1,2] shifts to arrive at **3pb′**-d_1 (cf. Scheme 4, bottom, and Scheme 5, bottom; see the Supporting Information for details). The fact that the deuteration grade in the homobenzylic position of **3pb′**-d_1 is marginal shows that a benzhydryl cation is thermodynamically strongly favored over a secondary *β*-silicon-stabilized carbenium ion.

These observations as well as DFT calculations using the M06-2X functional[18] support the mechanistic picture outlined in Scheme 6. The in situ-generated, benzene-stabilized silylium

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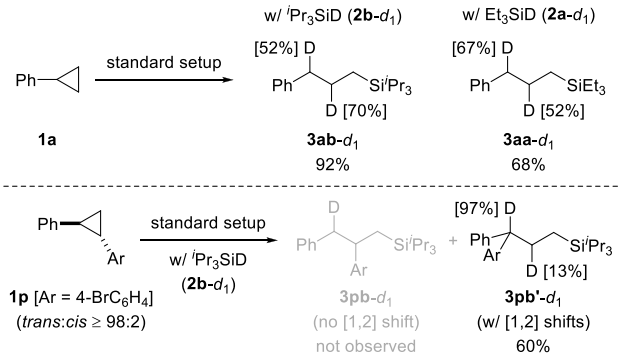
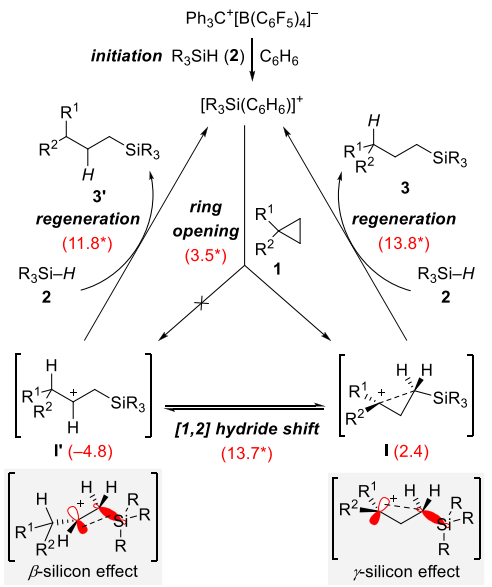
Scheme 5. Deuterium-Labeling Experiments[a]



[a]The deuteration grades were estimated by ^{1}H NMR spectroscopy.

Scheme 6. Mechanistic Picture[a]

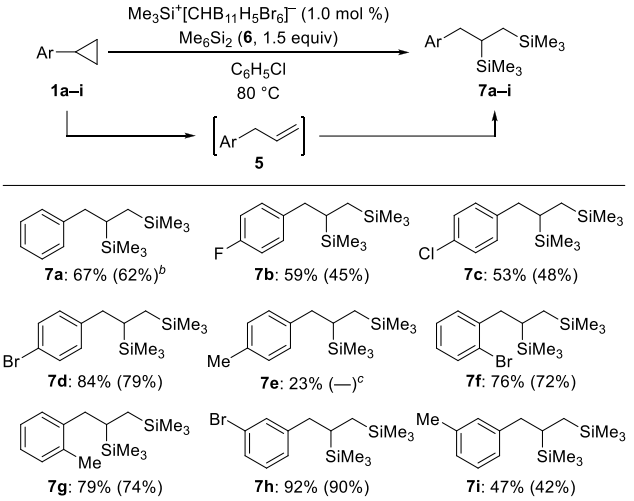


[a]Computed Gibbs free reaction energies and barriers (labeled with an asterisk) in kilocalories per mole are colored red (for **1a** with R^1 = Ph and R^2 = H and **2a** with R = Et). The computed Gibbs free energy profile and calculated structures of relevant intermediates and transition states are shown in the Supporting Information.

ion $[R_3Si(C_6H_6)]^+[B(C_6F_5)_4]^-$[19] opens the three-membered ring of **1** to form carbenium ion **I** over a low barrier of 3.5 kcal mol^{-1}; no transition state could be located for the direct transformation of **1** into **I′** (see the Supporting Information for details). With R^1 mostly being an aryl group, **I** is a benzylic carbenium that is further stabilized by the percaudal participation of the proximal Si–C(sp^3) σ-bond, i.e., by the γ-silicon effect. A Wagner–Meerwein rearrangement can convert **I** into carbenium ion **I′** that is now stabilized by the β-silicon effect; **I** and **I′** are in equilibrium by a [1,2] hydride shift over a barrier of 13.7 kcal mol^{-1}. Hydride transfer from the hydrosilane **2** to either of these intermediates affords products **3** and **3′** and regenerates the silylium-ion promoter. The activation barrier for the **I** → **3** hydride transfer (13.8 kcal mol^{-1}) is almost isoenergetic to the [1,2] hydride shift for **I** → **I′** (13.7 kcal·mol^{-1}), which is in excellent agreement with the outcome of the deuterium-labeling experiment shown in Scheme 5 (top, with Et_3SiD). These findings also suggest that γ- and β-silicon effects are in direct competition with each other[9] (see the Supporting Information for further analysis of the beneficial contribution of the γ-silicon effect).

Wang and co-workers had recently shown that $B(C_6F_5)_3$ catalyzes the isomerization of unactivated cyclopropyl to the corresponding allyl groups.[13a] A silylium ion can fulfill the same role in the absence of an external hydride source [**1** → **5** (Scheme 7); see the Supporting Information], and this set the stage for the use of cyclopropylbenzenes in our newly developed alkene disilylation with Me_6Si_2 (**6**) as the disilane reagent (Scheme 7).[16] Being catalyzed by 1.0 mol % $Me_3Si^+[CHB_{11}H_5Br_6]^-$, cyclopropylbenzenes **1a–i** were converted into the 1,2-bissilylated alkanes **7a–i**, respectively, in moderate to good yields. 1,1- and 1,2-disubstituted cyclopropanes as substrates did not react cleanly.

Scheme 7. Silylium-Ion-Promoted Cyclopropyl-to-Allyl Isomerization Followed by Alkene Disilylation[a]



[a]Yields determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard. Isolated yields after flash chromatography on silica gel in parentheses. [b]56% (52%) obtained at a 1 mmol scale. [c]Isolated yield not determined.

In summary, we demonstrated that silylium ions can promote the ring opening of unactivated cyclopropanes. With hydrosilanes as hydride sources, hydrosilylation with self-regeneration of the silylium ion take place. In the absence of a hydrosilane, isomerization of the cyclopropyl to an allyl group occurs, and the in situ-formed α-olefins can be directly reacted with hexamethyldisilane to furnish the 1,2-bissilylated alkane. All of these methods are transition-metal-free alternatives to C–C bond activation with transition metals.[20]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00173.

General procedures, experimental details, and characterization and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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