Cycloaddition

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Silylium-Ion-Promoted (5+1) Cycloaddition of Aryl-Substituted Vinylcyclopropanes and Hydrosilanes Involving Aryl Migration

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In memory of Professor Kilian Muñiz (1970–2020)

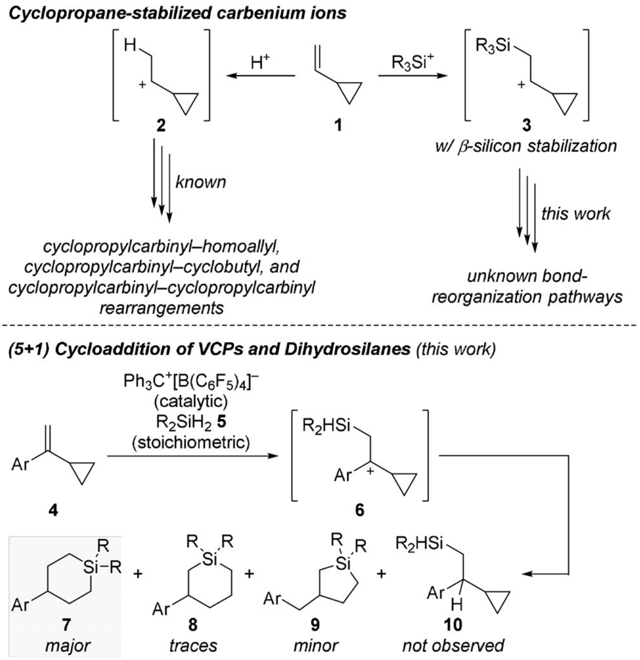
Abstract: *A transition-metal-free (5+1) cycloaddition of aryl-substituted vinylcyclopropanes (VCPs) and hydrosilanes to afford silacyclohexanes is reported. Catalytic amounts of the trityl cation initiate the reaction by hydride abstraction from the hydrosilane, and further progress of the reaction is maintained by self-regeneration of the silylium ions. The new reaction involves a [1,2] migration of an aryl group, eventually furnishing 4- rather than 3-aryl-substituted silacyclohexane derivatives as major products. Various control experiments and quantum-chemical calculations support a mechanistic picture where a silylium ion intramolecularly stabilized by a cyclopropane ring can either undergo a kinetically favored concerted [1,2] aryl migration/ring expansion or engage in a cyclopropane-to-cyclopropane rearrangement.*

Introduction

There is a rich chemistry associated with substituted vinylcyclopropanes (VCPs), especially because of their value as C5 synthons for the construction of complex carbon skeletons.[1] VCPs engage in a diverse set of bond reorganizations,[2] and transition-metal-catalyzed cycloadditions of VCPs continue to attract considerable attention.[3] Aside from those exciting synthetic applications, the parent VCP **1** aroused interest in carbocation chemistry as its protonation allowed the study of the stabilizing effect of the cyclopropyl group on carbenium ions.[4] The cyclopropylcarbinyl cation **2** is known to undergo various rearrangements (Scheme 1, top left),[2,4] and we asked ourselves what would happen upon treatment of **1** with a silylium ion instead of a strong Brønsted acid (Scheme 1, top right). The analogy lies in Fleming's early notion of silylium ions being fat protons,[5] and the result would likely be the carbenium ion **3** further stabilized by the β-silicon effect.[6] Assuming that the cyclopropane ring would not be directly opened by the silylium ion,[7] the fate of **3** would not be predictable, and we expected new chemistry to emerge. The plan was to initiate the reactions of the VCPs **4** and dihydrosilanes **5** with catalytic amounts of trityl borate $Ph_3C^+[B(C_6F_5)_4]^-$, relying on hydride abstraction (Corey reaction[8]) and, as such, self-regeneration of silylium ions.[7,9,10] Thus, carbenium ion intermediates such as **6**[11] would be captured by hydride. We chose the aryl-substituted VCPs **4** as model substrates and found several cyclic silanes (**7**—**9**) as products (Scheme 1, bottom) but no simple alkene hydrosilylation (**4**→**10**).[12] The six-membered-ring compound **7** is the result of a formal (5+1) cycloaddition accompanied by an unexpected migration of the aryl group. We present here the scope of the new reaction and its experimental and quantum-chemical mechanistic analysis.

Results and Discussion

Using catalytic amounts of $Ph_3C^+[B(C_6F_5)_4]^-$ as an initiator, we began our investigation with the reaction of **4a** and excess Et_2SiH_2 (**5a**) in benzene at ambient temperature (Table 1). The major product was the 4-phenyl-1-silacyclohexane **7aa** along with small quantities of the 3-phenyl-1-



Scheme 1. Cyclopropyl-substituted carbenium ions and their potential intermediacy in a silylium-ion-promoted (5+1) cycloaddition.

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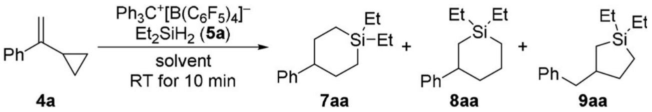
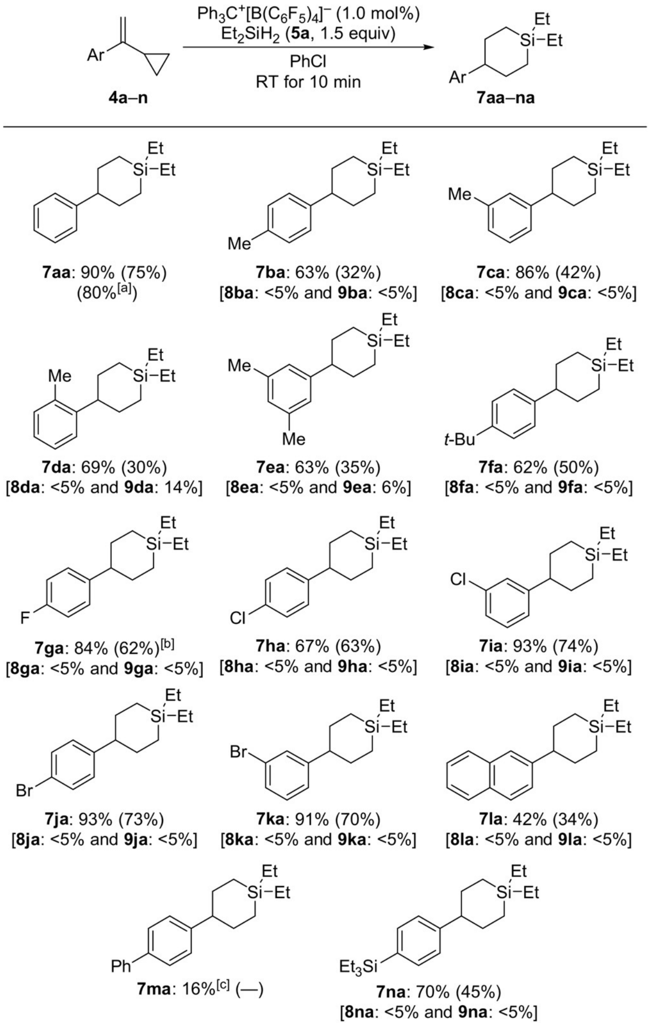
Table 1: Optimization of the trityl-cation-initiated (5+1) cycloaddition.[a]



Entry	Initiator (mol %)	Dihydrosilane (equiv)	Solvent	Yield [%][b]		
				7 aa	**8 aa**	**9 aa**
1	2.0	5.0	PhH	80	< 5	11
2	2.0	5.0	*o*-$C_6H_4Cl_2$	81	< 5	8
3	2.0	5.0	PhCl	90	< 5	6
4	1.0	5.0	PhCl	90	< 5	6
5	1.0	3.0	PhCl	90	< 5	5
6	1.0	1.5	PhCl	90	< 5	5
7	1.0	1.0	PhCl	75	9	5

[a] All reactions were performed with **4a** (0.25 mmol) and the indicated amounts of the initiator $Ph_3C^+[B(C_6F_5)_4]^-$ and Et_2SiH_2 (**5a**) under argon atmosphere in the indicated arene solvent (2.5 mL, 0.1 M) at room temperature. Conversion was greater than 95% for each entry as determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [b] Yields determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard.



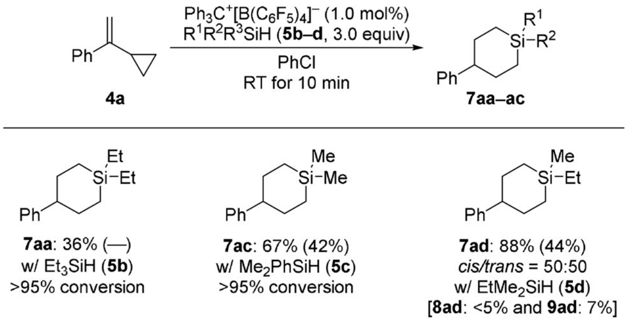
Scheme 2. Scope I: Variation of the aryl group in the VCPs **4** in the (5+1) cycloadditon with Et_2SiH_2. Unless otherwise noted, all reactions were performed on 0.25 mmol scale, and conversion was greater than 95% for each entry. Conversions and yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. Yields determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. Yields of analytically pure material obtained after flash chromatography on silica gel are given within parentheses. [a] Yield of isolated product on a 7.0 mmol scale. [b] $Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%) and Et_2SiH_2 (5.0 equiv) were used. [c] 82% **4m** was recovered.

silacyclohexane **8aa** and 3-benzyltetrahydrosilole **9aa** (entry 1). The arene solvent influenced the product distribution, and the formation of **9aa** was reduced in 1,2-dichlorobenzene and chlorobenzene (entries 2 and 3). Proceeding with chlorobenzene, we looked into the variation of other parameters (entries 4–6). Neither a lower catalyst loading (1.0 instead of 2.0 mol%) nor less dihydrosilane (5.0 to 1.5 equiv) had an effect on the reaction outcome. A slight decrease in yield and a somewhat less favorable product ratio was detected with equimolar quantities of the reactants (entry 7). The six-membered **7aa** did form in 90% yield under the optimized reaction conditions.

We then probed the substrate scope under the optimized protocol (Scheme 2). Electronic and steric modifications of the substituent on the aryl group were examined with **4a**–**k**. The parent VCP **4a** yielded **7aa** in 75% yield on a 0.25 mmol scale and in 80% yield on a 7.0 mmol scale. Substrates bearing, for example, electron-donating 4-methyl (**4b**), 3,5-dimethyl (**4e**), and 4-*tert*-butyl (**4f**) groups reacted smoothly, affording the desired products **7ba**, **7ea**, and **7fa**, respectively, in moderate yields. It is worthy of note that a methyl group in the *ortho* position, as in **4d**, did not affect the reactivity compared with **4b** and **4c**. Halogen atoms were tolerated well in this reaction, as shown for the cases with fluorine (**4g**), chlorine (**4h** and **4i**), and bromine (**4j** and **4k**) in the *para* or *meta* positions. The preparation of the *ortho*-substituted regioisomers had failed. A bulkier β-naphthyl group as in **4l** was also compatible with the reaction conditions although a lower yield was obtained. Conversely, the biphenyl-substituted **4m** hardly converted into the desired product **7ma**. We believe that the aryl substituents in **4l** and **4m** are more likely to engage in electrophilic aromatic substitution with silylium-ion intermediates,[13] thereby consuming the silylium ion to result in either decomposition or low conversion. A triethylsilyl group, as in **4n**, did not interfere with the (5+1) cycloaddition. The yields of the isolated products were generally low because of the challenging purification of these nonpolar compounds; yields refer to analytically pure material and come close to those determined by ^1H NMR spectroscopy with less rigor. We also note here that the reaction of a VCP with a cyclohexyl, instead of the phenyl group, led to a complex reaction mixture (not shown).

Aside from the dihydrosilane used above, we asked ourselves whether tertiary hydrosilanes would also participate in this reaction. We had recently shown that silylium ions can indeed cleave Si–C(sp^3) bonds.[14] This dealkylation corresponds to an exchange of an alkyl group between a quaternary silane and a silylium ion. Therefore, intermediates with no Si–H bond available anymore could potentially still engage in the self-regeneration of silylium ions.[7,9,10] The reactions summarized in Scheme 3 demonstrate the feasibility of the approach. Et_3SiH (**5b**) yielded the same product **7aa** as Et_2SiH_2 (**5a**) did in the reaction with **4a**. In turn, Me_2PhSiH (**5c**) underwent preferential dearylation, and $EtMe_2SiH$ (**5d**) showed that demethylation is favored over abstraction of an ethyl group. The observations are in line with those previously made.[14,15]

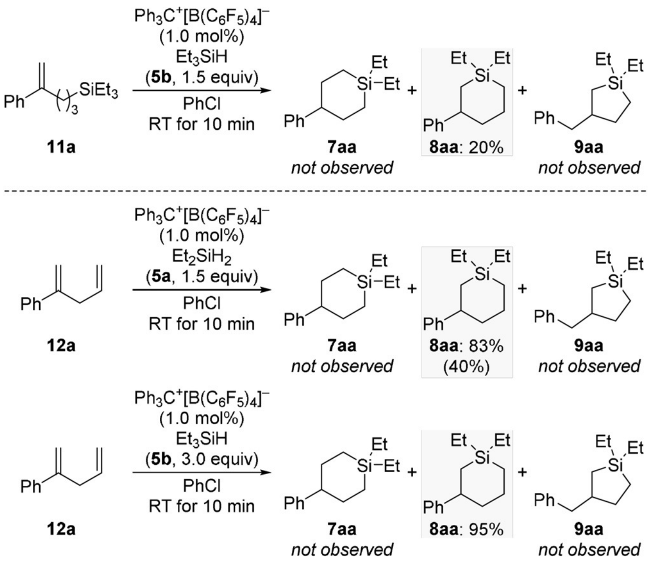
To gain insight into the reaction mechanism, a series of control experiments was designed (Schemes 4–6). We had recently shown that silylium ions promote the ring-opening hydrosilylation of cyclopropanes.[7] If the (5+1) cycloaddition begins with chemoselective ring opening of the cyclopropyl group in **4**, instead of the generation of the cyclopropyl-stabilized carbenium-ion intermediates **6** (cf. Scheme 1, bottom), the α-substituted styrene derivatives **11** will be likely intermediates. Hence, we prepared **11a** and subjected it to the standard procedure (Scheme 4, top). The *endo* cyclization did occur but without migration of the phenyl group, and **8aa** did form exclusively with no trace of **7aa**. This finding makes the ring-opening preceding functionalization of the alkene in the VCP unlikely. However, we also found that silylium ions can promote the isomerization of a cyclopropyl group into an allyl group.[7] We therefore prepared the 1,4-diene **12a** as another possible intermediate (Scheme 4, bottom). When reacted with either **5a** or **5b** it was again **8aa**, with no migration of the phenyl group, that was formed exclusively.[16] These results hint that transposition of the phenyl group occurs during the ring opening of cyclopropane.



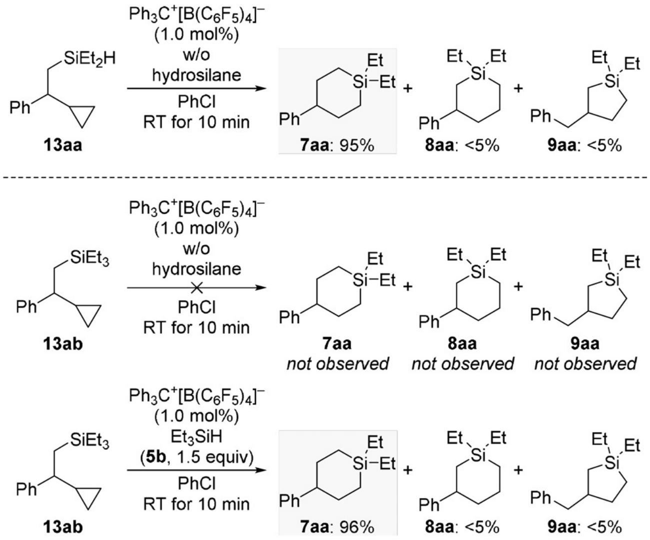
Scheme 3. Scope II: Variation of the hydrosilane **5** in the (5+1) cycloadditon with a VCP. Yields determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. Yields of analytically pure material obtained after flash chromatography on silica gel are given within parentheses.

We then turned towards the intermediates **13** with the cyclopropane ring still intact, that is, the alkene hydrosilylation products **13aa** and **13ab** of **4a** with **5a** and **5b**, respectively (Scheme 5). The assumed intermediate **13aa**, with a Si–H bond, underwent the ring expansion to **7aa** quantitatively with migration of the phenyl group when treated with 1.0 mol% of the trityl borate $Ph_3C^+[B(C_6F_5)_4]^-$ in the absence of an external hydrosilane (Scheme 5, top). The same result was obtained in the presence of **5b** (not shown). We concluded from this result that intramolecular hydrosilylation of the cyclopropyl group is interlinked with the aryl migration. Consequently, repeating this pair of reactions with presilylated cyclopropane substrate **13ab** with no Si–H bond led to the expected outcomes (Scheme 5, bottom). The trityl-cation-promoted ring expansion of **13ab** into **7aa** in the presence of **5b** likely involves the dealkylation of quaternary silanes recently described by us.[14] Hence, **13aa**→**7aa** with no hydrosilane and **13ab**→**7aa** with additional hydrosilane pass through the same silylium-ion intermediate.

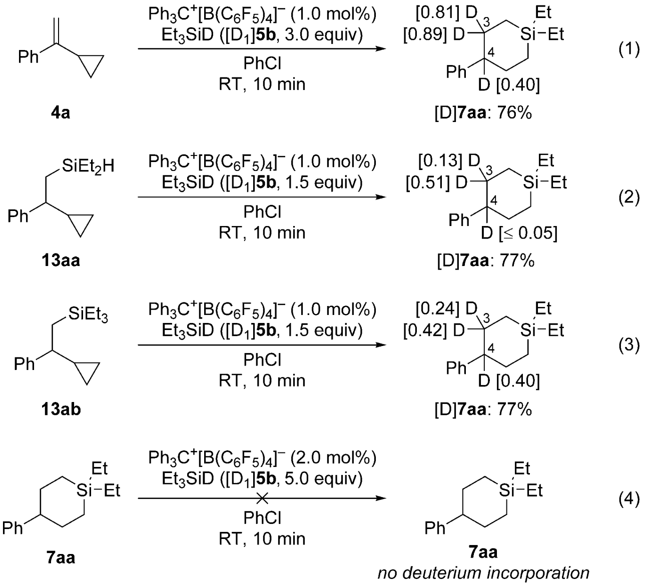
As shown in Scheme 6, a series of deuterium-labeling experiments was performed to further elucidate the mechanism. The deuterium incorporation was confirmed and estimated by ^{1}H and ^{2}H NMR spectroscopy (see the Supporting Information for details). When either **4a** or the presilylated **13ab** were reacted with Et_3SiD ([D$_1$]**5b**), deuterium atoms were found at C3 and C4 of the rearranged product



Scheme 4. Control experiments I: Verification of ring opening of the cyclopropyl group in VCPs prior to engagement of the alkene unit.



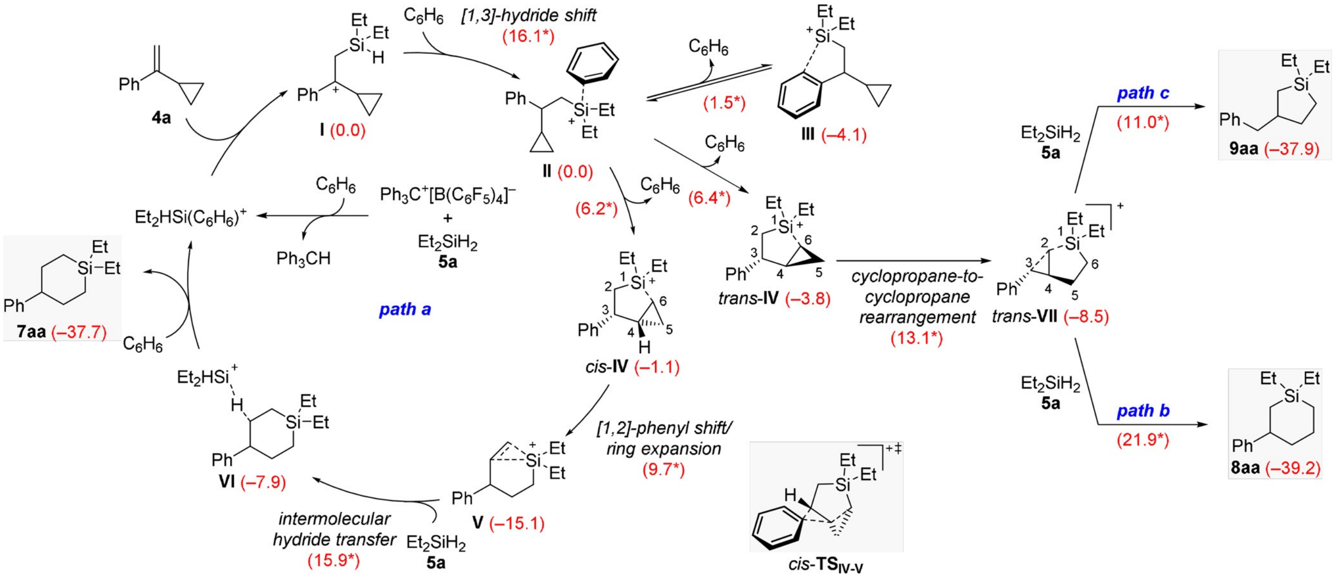
Scheme 5. Control experiments II: Cyclization experiments with presilylated cyclopropane intermediates, that is, alkene hydrosilylation products of VCPs.



Scheme 6. Control experiments III: Deuterium-labeling of the hydrosilane.

[D]**7aa** [Eq. (1) and Eq. (3)]. As shown in Scheme 5 (top), no additional hydrosilane is required to convert **13aa** into **7aa**. However, when this reaction was performed in the presence of Et_3SiD ([D_1]**5b**), deuterium incorporation was mainly found at C3 but hardly any at C4 of [D]**7aa** [Eq. (2)]. To exclude downstream deuteration at C4, we subjected **7aa** to the reaction conditions but did not detect any deuteration in the benzylic position [Eq. (4)]. Consequently, C−H bond formation occurs only during the migration/ring-enlargement sequence.

To elucidate the mechanistic details of this reaction, density-functional theory (DFT) calculations at the M062X/cc-PVTZ//M062X/6–311G(d,p) level[17] were performed on the model reaction of **4a** and **5a** with $Ph_3C^+[B(C_6F_5)_4]^-$ as the initiator (Scheme 7; see the Supporting Information for computational details and Figures S74–S79 for the free-energy profile and the optimized structures).[18] The solvent effect was taken into consideration using a polarizable continuum model (PCM)[19] with benzene as a solvent for both geometry optimizations and single-point energy calculations. Benzene was chosen over chlorobenzene because all byproducts did form in benzene. The initiation step involving hydride transfer from Et_2SiH_2 to Ph_3C^+ readily occurs over an activation barrier of 17.4 kcal mol^{-1}.[20] The resulting hydrogen-substituted silylium ion $[Et_2HSi(benzene)]^+$ can associate with the C=C double bond in **4a** to form the β-silicon-stabilized carbenium ion **I** with $[B(C_6F_5)_4]^-$ as the counteranion. This association has been calculated to be exergonic by 16.1 kcal mol^{-1} with respect to the ion pair $[Et_2HSi(benzene)]^+[B(C_6F_5)_4]^-$. In solution phase, the intermolecularly alkene-stabilized silylium ion **I’** is predicted to be more stable than other donor-stabilized silylium ions such as the corresponding benzene-, chlorobenzene-, hydrosilane-, or cyclopropyl-stabilized systems (see Tables S1–S3). Therefore, **I** was selected as the energy reference in the following discussion. The ion **I** then undergoes an intramolecular [1,3] hydride shift from the silicon atom to the benzylic carbon atom to arrive at the benzene-stabilized silylium ion **II** over a barrier of 16.1 kcal mol^{-1} (Scheme 7). Subsequent reorganization of **II** forms the intramolecularly stabilized silylium ions **III** (arene stabilization) or **IV** (cyclopropane stabilization in *cis*- or *trans*-configuration), and the corresponding barriers for the formation of these species are 1.5, 6.2, and 6.4 kcal mol^{-1} (relative to **II**). As a consequence of the low free-energy difference between these intermediates, they



Scheme 7. Initiation and catalytic cycle of the silylium-ion-promoted (5+1) cycloaddition of **4a** and **5a** (see the Supporting Information for calculated structures of relevant intermediates and transition states). For each reaction step, the Gibbs free reaction energies and barriers (labeled with an asterisk) in kcal mol^{-1} were computed with the M06-2X functional.

are all energetically accessible and likely in equilibrium with each other. The cyclopropane-stabilized **IV** can convert into the β-silicon-stabilized carbenium ion **V** through a concerted [1,2] phenyl shift/ring-expansion transition state (path a). Of the two configurations of **IV**, *cis*-**IV** gives the lowest [1,2] phenyl shift/ring-expansion transition state *cis*-$\mathbf{TS_{IV-V}}$ with a small activation barrier of 9.7 kcal mol^{-1} (see Figure S75 for further analysis of structural details of *cis*-$\mathbf{TS_{IV-V}}$ and *trans*-$\mathbf{TS_{IV-V}}$).[21] The [1,2] phenyl shift in *cis*-**IV** is driven by the ring expansion of the highly strained bicyclo[3.1.0]hex-2-silyl cation *cis*-**IV** into the six-membered-ring silylium ion **V**.[22] Subsequent hydride transfer from **5a** to **V** affords the C(sp^3)−H/silylium ion complex **VI** with a barrier of 15.9 kcal mol^{-1}. Finally, the association of another molecule of **4a** with Et_2HSi^+ regenerates **I** and releases **7aa**, that is the major product obtained experimentally. The [1,3] hydride shift with an activation barrier of 16.1 kcal mol^{-1} is the rate-limiting step (**I**→**II**), which is consistent with the rapid reaction rate at room temperature (see Figure S85).

The deuterium incorporation in the benzylic position of **7aa** (Scheme 6) could be attributed to the formation of the benzylic cation **7aa**$^+$ by an intramolecular [1,2] hydride shift in **V** (see Figure S84). Such a process is endergonic by 4.7 kcal mol^{-1} with an activation barrier of 14.6 kcal mol^{-1} (relative to **V**). Further deuteride transfer from [D$_1$]**5b** to **7aa**$^+$ forms [D]**7aa** and regenerates the donor-stabilized silylium ion. The corresponding barrier of this process is 13.9 kcal mol^{-1}.

The [1,2] aryl migration/ring expansion *cis*-**IV**→**V** of path a is in competition with the cyclopropane-to-cyclopropane rearrangement *trans*-**IV**→*trans*-**VII** (9.7 versus 13.1 kcal mol^{-1}; Scheme 7).[21] The formation of that bicylic cation is the result of synchronous C2–C4 bond making and C4–C6 bond breaking in *trans*-**IV**. A competing hydride transfer from **5a** to either C4 or C3 of *trans*-**VII** furnishes **8aa** (path b) and **9aa** (path c), respectively. The reaction outcome with **7aa** as the major product and **8aa** and **9aa** as byproducts is in accordance with the free-energy difference of those two barriers ($\Delta\Delta G^{\neq} = 3.4$ kcal mol^{-1}), making this (5+1) cycloaddition a kinetically controlled process.

Conclusion

We have disclosed here a transition-metal-free (5+1) cycloaddition of VCPs and hydrosilanes that is promoted by the self-regeneration of silylium ions.[7,9,10] The new reaction also involves a [1,2] migration of an aryl group, eventually furnishing 4- rather than 3-aryl-substituted silacyclohexane derivatives. Based on various control experiments and quantum-chemical calculations, reaction mechanisms that rationalize the formation of the three products have been proposed. The branching point is an intramolecularly cyclopropane-stabilized silylium ion that can either undergo a kinetically favored, concerted [1,2] aryl migration/ring expansion or engage in a cyclopropane-to-cyclopropane rearrangement. That bond reorganization represents a straightforward and atom-economic access to silacyclohexane derivatives, which are potentially relevant to medicinal applications.[23]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · density-functional calculations · ring expansion · silylium ions · small-ring systems

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[1] a) T. Hudlicky, J. W. Reed, *Angew. Chem. Int. Ed.* **2010**, *49*, 4864 – 4876; *Angew. Chem.* **2010**, *122*, 4982 – 4994; b) J. E. Baldwin, *Chem. Rev.* **2003**, *103*, 1197 – 1212.

[2] Z. Goldschmidt, B. Crammer, *Chem. Soc. Rev.* **1988**, *17*, 229 – 267.

[3] a) G. Fumagalli, S. Stanton, J. F. Bower, *Chem. Rev.* **2017**, *117*, 9404 – 9432; b) L. Souillart, N. Cramer, *Chem. Rev.* **2015**, *115*, 9410 – 9464; c) Y. Gao, X.-F. Fu, Z.-X. Yu, *Top. Curr. Chem.* **2014**, *346*, 195 – 231; d) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117 – 3179; e) S. C. Wang, D. J. Tantillo, *J. Organomet. Chem.* **2006**, *691*, 4386 – 4392.

[4] a) G. A. Olah, D. P. Kelly, C. L. Jeuell, R. D. Porter, *J. Am. Chem. Soc.* **1970**, *92*, 2544 – 2546; b) G. A. Olah, C. L. Jeuell, D. P. Kelly, R. D. Porter, *J. Am. Chem. Soc.* **1972**, *94*, 146 – 156; c) G. A. Olah, P. W. Westerman, *J. Am. Chem. Soc.* **1973**, *95*, 7530 – 7531; d) J. F. Wolf, P. G. Harch, R. W. Taft, W. J. Hehre, *J. Am. Chem. Soc.* **1975**, *97*, 2902 – 2904; e) H. Mayr, G. A. Olah, *J. Am. Chem. Soc.* **1977**, *99*, 510 – 513; f) K. B. Wiberg, D. Shobe, G. L. Nelson, *J. Am. Chem. Soc.* **1993**, *115*, 10645 – 10652.

[5] I. Fleming, *Chem. Soc. Rev.* **1981**, *10*, 83 – 111.

[6] a) J. B. Lambert, Y. Zhao, R. W. Emblidge, L. A. Salvador, X. Liu, J.-H. So, E. C. Chelius, *Acc. Chem. Res.* **1999**, *32*, 183 – 190; for a summary of the chemistry of silyl-substituted carbocations, see: b) H.-U. Siehl, T. Müller in *The Chemistry of Organic Silicon Compounds*, *Part 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1989**, pp. 595 – 701.

[7] A. Roy, V. Bonetti, G. Wang, Q. Wu, H. F. T. Klare, M. Oestreich, *Org. Lett.* **2020**, *22*, 1213 – 1216.

[8] J. Y. Corey, *J. Am. Chem. Soc.* **1975**, *97*, 3237 – 3238.

[9] a) J. B. Lambert, Y. Zhao, H. Wu, *J. Org. Chem.* **1999**, *64*, 2729 – 2736; b) V. J. Scott, R. Çelenligil-Çetin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852 – 2853; c) R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676 – 9682; d) K. Müther, M. Oestreich, *Chem. Commun.* **2011**, *47*, 334 – 336; e) K. Müther, J. Mohr, M. Oestreich, *Organometallics* **2013**, *32*, 6643 – 6646; f) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574 – 577; g) B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, *Science* **2017**, *355*, 1403 – 1407.

[10] For reviews of silylium-ion chemistry, see: a) J. C. L. Walker, H. F. T. Klare, M. Oestreich, *Nat. Rev. Chem.* **2020**, *4*, 54–62; b) P. Shaykhutdinova, S. Keess, M. Oestreich in *Organosilicon Chemistry: Novel Approaches and Reactions* (Eds.: T. Hiyama, M. Oestreich), Wiley-VCH, Weinheim, **2019**, pp. 131–170; c) V. Y. Lee, A. Sekiguchi in *Organosilicon Compounds*, *Vol. 1* (Ed.: V. Ya. Lee), Academic Press, Oxford, **2017**, pp. 197–230; d) T. Müller in *Structure and Bonding*, *Vol. 155* (Ed.: D. Scheschkewitz), Springer, Berlin, **2014**, pp. 107–162; e) T. Müller in *Science of Synthesis: Knowledge Updates 2013/3* (Ed.: M. Oestreich), Thieme, Stuttgart, **2013**, pp. 1–42.

[11] G. A. Olah, P. W. Westerman, J. Nishimura, *J. Am. Chem. Soc.* **1974**, *96*, 3548–3559.

[12] For a rare example of a hydrosilylation of VCPs without ring opening, see: A. G. Bessmertnykh, K. A. Blinov, Y. K. Grishin, N. A. Donskaya, I. P. Beletskaya, *Zh. Org. Khim.* **1995**, *31*, 49–53.

[13] S. Bähr, M. Oestreich, *Angew. Chem. Int. Ed.* **2017**, *56*, 52–59; *Angew. Chem.* **2017**, *129*, 52–59.

[14] a) Q. Wu, Z.-W. Qu, L. Omann, E. Irran, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2018**, *57*, 9176–9179; *Angew. Chem.* **2018**, *130*, 9317–9320; b) Q. Wu, A. Roy, E. Irran, Z.-W. Qu, S. Grimme, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2019**, *58*, 17307–17311; *Angew. Chem.* **2019**, *131*, 17468–17472.

[15] Q. Wu, E. Irran, R. Müller, M. Kaupp, H. F. T. Klare, M. Oestreich, *Science* **2019**, *365*, 168–172.

[16] The same result was obtained with $B(C_6F_5)_3$ as a catalyst: K. Shin, S. Joung, Y. Kim, S. Chang, *Adv. Synth. Catal.* **2017**, *359*, 3428–3436.

[17] a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241; b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157–167.

[18] We also computed the reaction of Et_3SiH (**5b**) instead of Et_2SiH_2 (**5a**). The rate-limiting step of this process is the intermolecular hydride transfer from Et_3SiH to the benzylic carbocation **I′** with a barrier of 19.8 kcal mol^{-1}. The corresponding catalytic cycle including the free-energy profile and the optimized structures are provided in the Supporting Information (see Scheme S3 and Figures S80–S83).

[19] J. Tomasi, M. Persico, *Chem. Rev.* **1994**, *94*, 2027–2094.

[20] L. Omann, B. Pudasaini, E. Irran, H. F. T. Klare, M. H. Baik, M. Oestreich, *Chem. Sci.* **2018**, *9*, 5600–5607.

[21] For each configuration of bicyclo[3.1.0]hex-2-silyl cation **IV** (*cis* or *trans*), the possibilities of both the [1,2] phenyl shift/ring expansion and the cyclopropane-to-cyclopropane rearrangement were systematically explored (see Figure S74 for energetic details). The *cis*-bicyclo[3.1.0]hex-2-silyl cation *cis*-**IV** gives an energetically lower [1,2] phenyl shift/ring-expansion transition state than its *trans*-isomer *trans*-**IV** ($\Delta G^{\neq} = 9.7$ versus 18.7 kcal mol^{-1}). In turn, *trans*-**IV** gives the energetically lowest transition state for the cyclopropane-to-cyclopropane rearrangement ($\Delta G^{\neq} = 13.1\ \text{kcal mol}^{-1}$ for *trans*-**IV** → **VII** as opposed to $\Delta G^{\neq} = 19.6\ \text{kcal mol}^{-1}$ for *cis*-**IV** → **VII**).

[22] T. Müller, C. Bauch, M. Ostermeier, M. Bolte, N. Auner, *J. Am. Chem. Soc.* **2003**, *125*, 2158–2168.

[23] For recent summaries, see: a) R. Ramesh, D. S. Reddy, *J. Med. Chem.* **2018**, *61*, 3779–3798; b) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2013**, *56*, 388–405; for original work, see: c) J. Wang, C. Ma, Y. Wu, R. A. Lamb, L. H. Pinto, W. F. DeGrado, *J. Am. Chem. Soc.* **2011**, *133*, 13844–13847.

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