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 ion. 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 CS 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)\(^1-4\) 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\(_3\)C[B(C\(_3\)F\(_7\))]\(^-\) 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\(_3\)C[B(C\(_3\)F\(_7\))]\(^-\) as an initiator, we began our investigation with the reaction of 4\(_a\) and excess Et\(_2\)SiH\(_2\) (5\(_a\)) in benzene at ambient temperature (Table 1). The major product was the 4-phenyl-1-silacyclohexane 7\(_{aa}\) along with small quantities of the 3-phenyl-1-

Cyclopropane-stabilized carbenium ions

\[ \text{known} \]

\[ \text{cyclopropylcarbinyl-homoaryl,} \]
\[ \text{cyclopropylcarbinyl-cyclobutyl, and} \]
\[ \text{cyclopropylcarbinyl-cyclopropylcarbinyl} \]
\[ \text{rearrangements} \]

\[ \text{(5+1) Cycloaddition of VCPs and Dihydrosilanes \textwłaściw (5+1) cycloaddition.} \]

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Scope I: Variations of the aryl group in the VCPs

ortho and para groups reacted smoothly, as an internal standard. Yields did form in 90% yield under the optimized reaction conditions. A slight decrease in yield and a somewhat less favorable product ratio was detected with 1.0 mol% of catalyst loading (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. We believe that the aryl substituents in the VCPs did not interfere with the reaction of a VCP with a cyclohexyl, instead of the phenyl group, led to a complex reaction mixture (not shown).

The preparation of the arenne 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 (4c), and 4-tert-butyl (4f) groups reacted smoothly, affording the desired products 7ba, 7ca, 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,[2] thereby consuming the silylium ion to result in either decomposition or low conversion. A triethylsilyl group, as in 4n, did 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 using CH$_2$Br$_2$ as an internal standard.

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.[34] 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

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**Table 1:** Optimization of the trityl-cation-initiated (5+1) cycloaddition

| Entry | Initiator (mol%) | Dihydrosilane (equiv) | Solvent | Yield [%] |
|-------|-----------------|-----------------------|---------|-----------|
| 1     | 2.0             | 5.0                   | PhH     | 80 < 5    |
| 2     | 2.0             | 5.0                   | o-C$_2$H$_5$Cl | 81 < 5 |
| 3     | 2.0             | 5.0                   | PhCl    | 90 < 5    |
| 4     | 1.0             | 5.0                   | PhCl    | 90 < 5    |
| 5     | 1.0             | 3.0                   | PhCl    | 90 < 5    |
| 6     | 1.0             | 1.5                   | PhCl    | 90 < 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$_3$C$^+$/B(C$_6$F$_5$)$_4^-$ and Et$_3$SiH$_2$ (5a) under argon atmosphere in the indicated arenne solvent (2.5 mL, 0.1 M) at room temperature. Conversion was greater than 95% for each entry as determined by $^1$H NMR spectroscopy using CH$_2$Br$_2$ as an internal standard. [b] Yields determined by $^1$H NMR spectroscopy using CH$_2$Br$_2$ as an internal standard.

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**Scheme 1.** Scope I: Variation of the aryl group in the VCPs 4 in the (5+1) cycloaddition with Et$_3$SiH$_2$. 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$_3$C$^+$/B(C$_6$F$_5$)$_4^-$ (2.0 mol%) and Et$_3$SiH$_2$ (5.0 equiv) were used. [c] 82% 4m was recovered.
self-regeneration of silylium ions.[7,9,10] The reactions summarized in Scheme 3 demonstrate the feasibility of the approach. Et₃SiH (5b) yielded the same product 7aa as Et₂SiH₂ (5a) did in the reaction with 4a. In turn, Me₂PhSiH (5c) went preferential dearylation, and EtMe₂SiH (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.

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 Ph₃C⁺[B(C₆F₅)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 ¹H and ²H NMR spectroscopy (see the Supporting Information for details). When either 4a or the presilylated 13ab were reacted with Et₃SiD ([D]₅), deuterium atoms were found at C3 and C4 of the rearranged product.
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 Et3SiD ([D]15b), 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.

\[
\text{Ph}_{3}C^+\left[B\left(C_{6}F_{5}\right)_{4}\right]^{-} \quad \text{(1.0 mol\%),} \\
\text{Et}_{3}SiD \quad \text{(3.0 equiv.)} \\
\text{PhCl} \\
\text{RT, 10 min} \\
\text{[D]7aa: 100%}
\]

\[
\text{Ph}_{3}C^+\left[B\left(C_{6}F_{5}\right)_{4}\right]^{-} \quad \text{(1.0 mol\%),} \\
\text{Et}_{3}SiD \quad \text{(1.5 equiv.)} \\
\text{PhCl} \\
\text{RT, 10 min} \\
\text{[D]7aa: 77%}
\]

\[
\text{Ph}_{3}C^+\left[B\left(C_{6}F_{5}\right)_{4}\right]^{-} \quad \text{(1.0 mol\%),} \\
\text{Et}_{3}SiD \quad \text{(1.5 equiv.)} \\
\text{PhCl} \\
\text{RT, 10 min} \\
\text{[D]7aa: 77%}
\]

\[
\text{Ph}_{3}C^+\left[B\left(C_{6}F_{5}\right)_{4}\right]^{-} \quad \text{(2.0 mol\%),} \\
\text{Et}_{3}SiD \quad \text{(5.0 equiv.)} \\
\text{PhCl} \\
\text{RT, 10 min} \\
\text{7aa: no deuterium incorporation}
\]

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

\[\text{[D]7aa} \quad \text{[Eq. (1) and Eq. (3)]}\]

To elucidate the mechanistic details of this reaction, density-functional theory (DFT) calculations at the M062X/cc-PVTZ//M062X/6–311G(d,p) level\cite{17} were performed on the model reaction of 4a and 5a with Ph3C’+[B(C6F5)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).\cite{18} The solvent effect was taken into consideration using a polarizable continuum model (PCM)\cite{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 Et2SiH2 to Ph3C+ readily occurs over an activation barrier of 17.4 kcal mol\(^{-1}\).\cite{20} The resulting hydrogen-substituted silylium ion [Et2SiH(benzene)]+ can associate with the C=C double bond in 4a to form the β-silicon-stabilized carbenium ion I with [B(C6F5)4]– as the counterion. This association has been calculated to be exergonic by 16.1 kcal mol\(^{-1}\) with respect to the ion pair [Et2SiH(benzene)]+[B(C6F5)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...
are all energetically accessible and likely in equilibrium with each other. The cyclopropane-stabilized IV can convert into the β-silicon-stabilized carbenium ion IV 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-IV with a small activation barrier of 9.7 kcal mol⁻¹ (see Figure S75 for further analysis of structural details of cis-IV and trans-IV). Subsequent hydride transfer from 5a to V affords the C(sp³)-H/siliconium ion complex VI with a barrier of 15.9 kcal mol⁻¹. Finally, the association of another molecule of 4a with Et₃HSi⁺ 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 V at 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]-5b to 7aa forms [D]-7aa and regenerates the donor-stabilized siliconium 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). 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 (ΔAG° = 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 silicons ions. 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 siliconium 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.

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Conflict of interest

The authors declare no conflict of interest.

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

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[18] We also computed the reaction of Et₃SiH (5b) instead of Et₂SiH₂ (5a). The rate-limiting step of this process is the intermolecular hydride transfer from Et₃SiH to the benzylic carbocation 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).

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