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Me₃SiSiMe₂(OⁿBu): a disilane reagent for the synthesis of diverse silacycles *via* Brook- and retro-Brook-type rearrangement[†]

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Herein, a readily available disilane Me₃SiSiMe₂(O^{n} Bu) has been developed for the synthesis of diverse silacycles *via* Brook- and retro-Brook-type rearrangement. This protocol enables the incorporation of a silylene into different starting materials, including acrylamides, alkene-tethered 2-(2-iodophenyl)-1*H*-indoles, and 2-iodobiaryls, *via* the cleavage of Si–Si, Si–C, and Si–O bonds, leading to the formation of spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles in moderate to good yields. Preliminary mechanistic studies indicate that this transformation is realized by successive palladium-catalyzed bis-silylation and Brook- and retro-Brook-type rearrangement of silane-tethered silanols.

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Introduction

Silacycles have attracted increasing attention because they have shown unique physical, optoelectronic, and physiological properties in medicinal chemistry and materials science.¹ In this context, considerable efforts have been devoted to the development of synthetic methods for silacycles, which is a prerequisite for fully discovering their application potentials.^{2,3} Among them, of particular interest to synthetic chemists is the synthesis of silacycles *via* the cleavage of C–Si bonds.³ Typical strategies include direct annulation of silicon-based frameworks^{3*a*-*n*} and C–Si/C–C bond exchange reaction of small ring systems based on the existence of a high ring strain.^{3*a*-*r*} However, these methods generally require transition-metal catalysts to assist the activation of C–Si bonds. Transitionmetal-free catalyzed annulation to assemble silacycles by cleaving C–Si bonds is still elusive so far.

The Brook rearrangement enables an intramolecular migration of a silyl group from carbon to oxygen atoms *via* a hypervalent silicon species,⁴ which was initially introduced by Brook⁵ and was demonstrated to be a reversible process.⁶ Its reverse process, namely retro-Brook rearrangement, can, in turn, be achieved by the transfer of a silyl group from oxygen to carbon atoms (Scheme 1A).⁷ Obviously, the Brook and retro-

The cleavage of SI-SI, SI-O, and SI-C bonds * Divergent synthesis Scheme 1 (A) Brook and retro-Brook rearrangement. (B) The Known reaction modes of disilanes. (C) Our work: a disilane reagent Me₃-SiSiMe₂(OⁿBu) for the synthesis of diverse silacycles.





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Brook rearrangements allow the cleavage of a C–Si bond and the formation of a C–Si bond under transition-metal-free catalysis.⁸ On the other hand, the existing studies are limited to the translocation of a single silyl group from the starting materials. The migration of two different silyl groups in one event has not been reported so far. In this context, we want to explore the synthesis of silacycles *via* the migration of two different silyl groups in the Brook and retro-Brook rearrangement. The design and synthesis of silane-tethered silanols is undoubtedly the primary task and challenge to achieve this hypothesis.

Disilanes have been among the most versatile silvlation reagents in organic synthesis. Over the past few decades, a myriad of methods for accessing organosilanes from disilanes have focused on the activation of Si-Si bonds for the development of mono-silvlation involving aryl halides or cyanides, alkenes, and C-H bonds and bis-silvlation of alkynes, alkenes, carbenes, and palladacycles (Scheme 1B).9-13 Particularly, the pioneering work that realizes the bis-silvlation of in situ generated palladacycles with hexamethyldisilane via the cleavage of Si-Si bonds has recently been reported by Zhang, Cheng, and us.12,13 These advances have inspired us to modify hexamethyldisilane, namely the replacement of the methyl group with an oxygen-containing group, for the synthesis of silane-tethered silanols, which were further converted into silacycles via Brook and retro-Brook-type rearrangement. Herein, we disclose a Brook and retro-Brook-type rearrangement strategy for the synthesis of diverse silacycles, including spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles, by employing a readily available disilane reagent Me₃SiSiMe₂(- $O^{n}Bu$) that could be prepared by a simple treatment of pentamethylchlorodisilane with n-butanol in the presence of NEt₃ at room temperature (Scheme 1C). Notably, the cleavage of Si-Si, Si-C, and Si-O bonds is involved in the transformation.

Results and discussion

We initiated the studies by investigating the reaction of acrylamide **1a** with 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a**. To our delight, the anticipated spirobenzosilole **3a** was indeed afforded in 66% yield by using a simple catalytic system composed of Pd(OAc)₂ and K₂CO₃ in DMF at 90 °C. Encouraged by these initial results, various parameters were screened, and the optimized reaction conditions are as follows: **1a** (0.2 mmol),



Scheme 2 Screening of disilanes (2).

2a (0.3 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), and K_2CO_3 (0.6 mmol) in DMA (2 mL) at 90 °C under N_2 for 6 h (see the ESI[†] for details). Next, several disilanes **2b-h** were tested. As shown

in Scheme 2, when the *n*-butyl group of disilane 2a was replaced by other functional groups such as *n*-hexyl, benzyl, cyclohexyl, and 2-oxopropyl, all of them could afford the desired product **3a**, albeit in a lower yield. Unexpectedly, disilane **2f** was unreactive. Finally, disiloxane **2g** was found to produce product **3a** in 58% yield.

With the optimal reaction conditions and disilane reagent confirmed, the scope of acrylamides **1** was subsequently examined. Gratifyingly, this protocol was applicable to a large variety of acrylamides **1** to afford spiro[benzo[*b*]silole-3,3'indolin]-2'-ones **3a–u** in moderate to good yields (Scheme 3). Note that the replacement of iodine atoms with bromine atoms on the acrylamide showed good reactivity, delivering the product **3a** in 66% yield. Moreover, the three substructures of acrylamides **1** were systematically investigated. Regarding different substituents on the nitrogen atom, methyl or ethyl group substituted acrylamides **1b** and **1c** were competent substrates, while acrylamide **1d** with a Ts group could not give the target product **3d** under the standard conditions. For the 2iodoaniline fragment, a broad range of functional groups on the



Scheme 3 Variations of the acrylamides (1). ^aReaction conditions: 1 (0.2 mmol), 2a (0.3 mmol), Pd(OAc)₂ (10 mol%), PPh₃ (20 mol%), K₂CO₃ (3 equiv.), and DMA (2 mL) at 90 °C under a N₂ atmosphere for 6 h. ^bN-Benzyl-N-(2-bromophenyl)-2-phenylacrylamide. ^c1a (1 mmol). ^d70 °C and 1 h.

benzene ring, including electron-donating groups (Me and OMe), modifiable halogen groups (F and Cl), and even strong electron-withdrawing groups (CF₃, CO₂Me, and NO₂), were well tolerated (3e-n). Meanwhile, the structure of 3g was unambiguously confirmed by X-ray crystallography. Their electronic properties seem to affect the reactivity, since substrates 11-n with strong electron-withdrawing groups, especially CO2Me and NO₂ groups, resulted in a diminished yield. Finally, the compatibility was further demonstrated by testing the key 2phenylalkene moiety. Both the benzene ring containing ortho or para substituents and the naphthalene ring could survive, affording spirobenzosilole 30-u in moderate to good yields. Nevertheless, a slight modification of the reaction conditions was required when substrates bearing F groups were used (3q and 3t). When the reaction was scaled up to 1 mmol, 70% spirocyclic product 3a could also be obtained.

To highlight the generality of this domino Heck/ silacyclization, we envision that fused benzosiloles can be synthesized by a domino Heck/ortho C-H functionalization of aryl iodides. Therefore, 2-(2-iodophenyl)-1-(2-methylallyl)-1Hindole was employed to react with disilane 2a under the above reaction conditions. To our delight, indolo[2,1-a]silolo[4,3,2-de] isoquinolines 5a could smoothly be produced in 58% yield by the cleavage of Si-Si and Si-O bonds. Encouraged by these results, the scope of 2-(2-halophenyl)-1-(2-methylallyl)-1Hindoles was then explored (Scheme 4). Bromine atoms instead of iodine atoms on the substrate 4a' were subjected to the standard conditions, which could give product 5a, albeit in a lower yield. Satisfactorily, substrates 4b-g being diversely substituted (Me, F, and Cl) on the indole ring were able to undergo this domino Heck/silacyclization with disilane 2a to provide the desired products 5b-g in moderate yields. Differently, using substrate 4h required relatively mild conditions.

> Pd(OAc)₂ (10 mol%) PPh₃ (20 mol%)

> > K₂CO₃ (3 equiv)

DMA, 90 °C, N₂, 6 h

5c. 50 %

5h. 40%



5a. 42%

5b. 45%



Scheme 5 Variations of the 2-iodobiphenyls (6). ^aReaction conditions: 6 (0.2 mmol), 2a (0.24 mmol), Pd(OAc)₂ (10 mol%), K₂CO₃ (3 equiv.), and DMF (2 mL) at 90 °C under a N₂ atmosphere for 12 h. ^b2-Bromobiphenyl was used. ^c2-lodo-4'-methyl-1,1'-biphenyl was used. ^d2lodo-3'-methyl-1,1'-biphenyl was used.

To emphasize the versatility of the disilane reagent Me₃-SiSiMe₂(O^{*n*}Bu), we next attempted to synthesize π -conjugated dibenzo[b,d]siloles by performing the reaction of 2-iodo-1,1'biphenyl with $Me_3SiSiMe_2(O^nBu)$ 2a. However, no anticipated product was observed under the above standard conditions. Subsequently, PPh₃ was found to suppress the reaction, since dibenzo[b,d]siloles 7a could be afforded in 52% yield by the removal of PPh₃. Encouraged by these results, the optimal reaction conditions that could furnish 64% of 7a were established by the screening of various parameters (see the ESI[†] and Scheme 5). Afterward, a series of substituted 2-iodobiphenyls were examined. Delightfully, the electron-donating group (Me and OMe) on the benzene ring could be tolerated for the silacyclization reaction with disilane 2a, thus delivering the desired products 7b-k in moderate yields. Unfortunately, this protocol was not applicable to substrates 61-o bearing an electronwithdrawing group. The possible reason is that the protonation of palladacycles formed by substrates 61-o is easier than bis-silulation (see the ESI[†]).

To gain insight into the reaction mechanism, a range of control experiments were performed (Scheme 6). The reaction of acrylamides 1a with disiloxane 2h or 2i could afford product 3a in 27% and 50% yields, respectively, under the optimal reaction conditions (eqn (1)[†]). Moreover, hexamethyldisiloxane (TMSOTMS) was detected by gas chromatography in the model reaction of 1a with 2a (eqn (2), see the ESI[†]). These results indicated that the silicon source of product 3a came from the dimethylsilyl group generated by disilane 2a via the cleavage of Si-Si and Si-O bonds. Interestingly, two disilylated products 8a and 8a' as well as product 3a were isolated in 43%, 27%, and 16% yields when 1a and 2a were reacted under the standard conditions for 20 minutes (eqn (3)[†]). Therefore, we speculated that two disilylated products 8a and 8a' were the reaction intermediates (the structure of 8a was absolutely confirmed by X-ray crystallography). Finally, a spiropalladacycle¹⁴ that could

5a, 58% (35%)¹

5f. 44%



be prepared from acrylamides and stoichiometric $Pd(PPh_3)_4$ was employed for the reaction with disilane **2a** (eqn (4)†). Unexpectedly, no product **3b** was observed in the absence of $Pd(OAc)_2$ and PPh_3 . Surprisingly, extra addition of $Pd(OAc)_2$ and PPh_3 could give product **3b** in 60% yield. These results suggested that the spiropalladacycle as a reaction intermediate underwent transmetalation with intermediate **G**, rather than direct oxidative addition with disilane **2a**, to furnish disilylated products **8a** and **8a'**, which were then converted into the desired product **3a**.

To verify our hypothesis and propose the possible formation process of **3a** from **8a** or **8a**', we conducted several control experiments (Scheme 7). The silacyclization of disilylated products **8a** and **8a**', respectively, was conducted in the absence



Scheme 7 Mechanistic experiments. The possible process for the transformation of 8a and 8a' into 3a.

of $Pd(OAc)_2$ and PPh_3 , and the product **3a** was obtained in 66% and 60% yields as expected (eqn (1)[†]). Besides, TMSOTMS was also detected (see the ESI[†]). These results demonstrated that the transformation of 8a and 8a' into 3a involved the cleavage of the Me₃Si-C bond, which did not require the assistance of palladium catalysts. On the basis of these results from eqn (1)[†] and previous work reported by Smith and Takeda,15 we speculated that 8a and 8a' undergo a Brook- and retro-Brook-type rearrangement to afford 3a (path c and path d). To capture carbanion species F and F', two common electrophilic reagents, such as iodomethane and benzyl bromide, were added for the silacyclization of 8a and 8a' (eqn (2) and (3)[†]). However, the corresponding products F-1 and F'-2 were not observed. Therefore, these results are more favorable to this pathway involving synergetic Brook/retro-Brook-type rearrangement (path d).

Based on the results of mechanistic experiments as well as reported work,12,13,15 a plausible mechanism for the synthesis of silacycles was proposed (Scheme 8). Initially, oxidative addition followed by intramolecular Heck-cyclization of acrylamides 1a to Pd(0) species forms intermediate A, which then undergoes a C-H activation to afford spiropalladacycle B. Next, spiropalladacycle B produces disilylated products 8a/8a' and regenerates Pd(0) by sequential transmetalation with intermediate G generated by disilane 2a, reductive elimination and further hydrolysis (path a). 8a and 8a' then undergo a synergetic Brook/retro-Brook-type rearrangement to afford 3a and a trimethylsiloxy anion, which could be converted into TMSOTMS (path d).¹⁶ Notably, another possible pathway that synthesizes disilylated products 8a/8a' by direct oxidative addition of spiropalladacycle B with disilane 2a is ruled out by the results of eqn (4)† (path b).



Scheme 8 Possible reaction mechanism.

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Conclusions

In conclusion, we have disclosed the first example of divergent synthesis of silacycles *via* a Brook- and retro-Brook-type rearrangement strategy by employing a readily accessible disilane reagent Me₃SiSiMe₂(O^{*n*}Bu). In this novel transformation, divergent silacycles, such as spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles, can be produced in moderate to good yields by an unprecedented complex process composed of a bis-silylation of a palladacycle and a Brook- and retro-Brook-type rearrangement. Notably, mechanistic studies reveal that bis-silylation of the palladacycle is completed by a transmetalation process. Further applications of the disilane reagent Me₃SiSiMe₂(O^{*n*}Bu) and the rearrangement are still in progress in our laboratory.

Data availability

All experimental procedures and spectroscopic data can be found in the ESI.†

Author contributions

Y. X. designed and performed the experiments and analysed the data. W. X., X. C., X. L., H. L., M. Z., X. Y. and G. D. contributed to data analysis and scientific discussion. Y. Y. and Y. L. supervised the project, analyzed the results and wrote the manuscript.

Conflicts of interest

The authors declare no competing interests.

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