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Silylium ion-promoted dehydrogenative cyclization: synthesis of silicon-containing compounds derived from alkynes†‡

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Treatment of dialkylbenzylsilane (1) with trityl tetrakis(pentafluorophenyl)borate (TPFPB) in the presence of terminal or internal alkynes (3) and 2,6-di-*tert*-butyl-4-methylpyridine gave the corresponding 1,2-dihydro-2-silanaphthalene derivatives (4) in 34–82% yields.

Lewis acids are often utilized as reactants or catalysts to activate inert multiple bond-containing compounds in organic syntheses. A sextet silvlium ion¹ with a vacant p-orbital has an intrinsically high electrophilicity and can interact with π -donor nucleophiles such as alkenes, alkynes, and aromatic compounds, as well as ketones with a coordinative lone pair of electrons.^{2,3} In contrast to exergonic bond formation with a carbocation, an electronically positive silicon center tends to bind to Lewis bases reversibly, so it has the potential to play the role of a catalyst 4^{4-8} as well as a high reactive reagent.9 The silvlium ion, which is derived from treatment of the corresponding hydrosilane with the trityl cation, exists usually as silane¹⁰ or arene adducts^{2e} and permits the transition metal-free consecutive hydrosilylation of unsaturated compounds.⁴ Oestreich et al. have reported that the unique silylium ion bearing the ferrocenyl group undergoes a catalytic [4+2] cycloaddition with dienes or α,β -unsaturated carbonyl compounds.6d

Recently, Müller and coworkers have successfully introduced carbon dioxide activated by the simple trialkylsilylium ion into an aromatic ring through electrophilic substitution.^{9a} These facts prompted us to develop a silylium ion-promoted Friedel–Crafts reaction with unsaturated compounds, *i.e.*, it was hypothesized that the β -silyl cations derived by the addition of silylium

ions to the X–Y π -bonds allow electrophilic substitution on the aromatic ring.

Kawashima *et al.* have synthesized dibenzosilole and trisilasumanene derivatives through the sila-Friedel–Crafts reaction, where the silylium ion forms a five-membered π -complex with an intramolecular aromatic moiety and consequent deprotonation of the π -complex with 2,6-lutidine produces the dibenzosilole derivatives.¹¹ Herein, we decided to use dialkylbenzylsilanes (R₂BnSiH, **1**), in which case solvent-coordinated silylium ions [R₂BnSi-arene]⁺ (2) interact with the appropriate unsaturated compounds to give the β -silyl cations. They undergo intramolecular electrophilic substitution to the benzyl group to afford the corresponding 6-membered ring compounds (Scheme 1). In this report, we describe the reactions of the silylium ions derived from **1** with alkynes followed by intramolecular aromatic electrophilic substitution reactions of the resulting ethenyl cations.

A solution of trityl tetrakis(pentafluorophenyl)borate (TPFPB) in benzene was slowly added to a benzene solution of benzyldimethylsilane (1a), a base and trimethylsilylacetylene (3a) to give the 1,2-dihydro-2-silanaphthalene derivative (4aa) except for the case in entry 3, in which a mixture of 4aa and 1,2,3,4-tetrahydro-2-silanaphthalene 5aa was obtained (Scheme 1, details of method A are provided in the ESI‡). Among bases that were examined (Table 1, entries 1–4), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) gave the best result, namely, a sila-cycle 4aa was obtained as a colorless oil in 58% isolated yield. The regiochemistry of 4aa was determined by correlation of the ethenyl proton with the ipso carbon on the aromatic ring in an HMBC experiment. The sterically small bases such as 2,6-lutidine and the proton sponge relative to DTBMP were less effective for the dehydrogenative



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 $[\]dagger$ This work is dedicated to Professor Renji Okazaki on the occasion of his 77th birthday.

[‡] Electronic supplementary information (ESI) available: Experimental section, the spectroscopic data and crystallographic data. CCDC 989789 for **4ab** and 989790 for **4ae**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01648c

 Table 1
 Optimization of dehydrogenative cyclization using hydrosilane 1a

 and trimethylsilylacetylene (3a)



 a 2,6-Lut = 2,6-lutidine, proton sponge = 1,8-bis(dimethylamino)-naphthalene, DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine. b Isolated yields based on **1a**. c Not detected.

cyclization because they may coordinate to the resulting silylium ion 2a to interrupt the addition of alkyne.¹² In entry 3, use of Cs_2CO_3 resulted in the formation of a mixture of 4aa and 5aa. As a result of optimizing the reaction conditions, the isolated yield of 4aa was increased up to 73% upon addition of 1a to the benzene solution of TPFPB, DTBMP, and 3a (method B) (entry 5).

Compound 5aa is considered to be formed by hydride abstraction of the protonated 4aa from the Si-H bond of 1a. Silvlium ion-promoted catalytic hydrosilylation of various unsaturated compounds such as alkenes, alkynes, ketones, and imines has been reported,⁴ and it is thought that the unsaturated compound activated by addition of the silvlium ion abstracts the hydride from the hydrosilane to afford the hydrosilylation product and regenerates the silvlium ion. Therefore, the above formation mechanism for 5aa seems to be reasonable. In the present stoichiometric reaction using 1a and 3a, the cation center of the transient ethenyl cation A could approach the intramolecular benzyl group, and the subsequent Friedel-Crafts reaction via cyclohexadienyl cation B resulted in the formation of 4aa (Scheme 2). Interestingly, when 3a was used as an alkyne, the isomer with the trimethylsilyl group at the 3-position was predominant because two silyl groups can stabilize the β-cation



Scheme 2 Plausible mechanism for the formation of **4** from hydrosilane **1** and alkynes **3**.

Table 2	Dehydrogenative cyclization using hydrosilanes 1a,b with alkynes
a−q ^a	



^{*a*} Using method B. ^{*b*} Isolated yields based on 1. ^{*c*} Complex mixture. ^{*d*} Using method A. ^{*e*} Benzyldimethyl(2-phenylethynyl)silane (**6ag**) was obtained in 54% yield.

(the β -effect of a silyl group). However, the cationic oligomerization of the alkyne with the ethenyl cation **A** was not completely prohibited under these conditions, which caused a decrease in the yields of the sila-cycle **4aa**.

Using the optimized method B, the scope of hydrosilanes 1 and alkynes 3 was examined and the results are summarized in Table 2.¹³ The cyclization using hydrosilane **1a** and phenylacetylene (3b) or 1-hexyne (3c) except for trimethylsilylacetylene (3a) as a terminal alkyne (entries 1-4) gave the corresponding 4-substituted 1,2-dihydro-2-silanaphthalene 4ab or 4ac, indicating that the secondary ethenyl cation in A is more stable than the primary one. X-ray crystallographic analysis of 4ab showed that the C(3)–C(4) bond is a double bond (1.347(2) Å) and that the phenyl group is located on the C(4) atom (Fig. 1). The presence of the tert-butyl group prohibited the formation of 4ad (entry 4), as expected, because of its steric hindrance for intramolecular electrophilic substitution of the benzyl group. Müller et al. have reported that ethenyl cations bearing tert-butyl or aromatic groups at the α -position and two silvl groups at the β -position can be isolated and are stable even in benzene.¹⁴ The remarkable stability of the isolated ethenyl cations seems to be attributable to the β-effect by two silyl groups and steric hindrance of the α -substituent. In our system, most of the resulting ethenyl cations maintain the moderate electrophilic reactivity so that aromatic substitution can occur, in contrast to the Müller's system. Internal alkynes such as diphenylacetylene (3e) and 3-hexyne (3f) also yielded the corresponding cyclization products in 77% and 34% isolated yields for 4ae and 4af, respectively (entries 5 and 6). The crystal structure of 4ae was revealed to be similar to that of 4ab, except for the phenyl group at the 3-position in the 1,2-dihydro-2silanaphthalene backbone (Fig. S1, ESI[‡]). The good yield for the annulation of sterically bulky diphenylacetylene is attributed to a prohibition of alkyne oligomerization by the resulting



Fig. 1 Crystal structure of one of the two independent molecules in **4ab**, showing 50% probability of thermal ellipsoids.

ethenyl cation. Use of phenyl(trimethylsilyl)acetylene (**3g**) gave the phenylethynylation product (**6ag**) in 54% isolated yield with no observation of **4ag** (entry 7) since an electropositive silicon atom in the trimethylsilyl group allows the nucleophilic attack of DTBMP, resulting in the desilylation reaction to give **6ag**.

To elucidate the steric effect of the substituent on the silicon center, we performed the reactions of **1b** possessing two isopropyl groups on the silicon atom with alkynes (entries 8–12). The dehydrogenative cyclization with alkynes occurred in moderate-to-good yields except for 3-hexyne (**3f**), although the cyclization using **1b** required a longer reaction time (30 min) than that required using **1a** (15 min). The product yield for the reaction of **1b** with **3b** or **3c** improved compared with that of **1a**, which can be understood by the Thorpe–Ingold effect.¹⁵ The regioselectivity for the cyclization was maintained despite the sterically bulky isopropyl group on the silicon atom.

Application of the stoichiometric system to a catalytic one is important from the viewpoint of reduction of waste. Considering the aforementioned formation mechanism of **5aa**, shown



Scheme 3 Plausible catalytic cycle for the formation of 5 from hydrosilane 1 and alkynes 3.



Scheme 4 Catalytic cyclization using hydrosilane 1 and alkyne 3c.

in entry 3 of Table 1, the catalytic cycle as shown in Scheme 3 can be designed. That is, silylium ion 2 formed from 1 is reacted with alkyne 3 to give cyclohexadienyl cation **B**. Then, carbocation **C** formed by the H-migration and aromatization from cyclohexadienyl cation \mathbf{B}^{16} abstracts the hydride from the Si-H bond of 1 to produce 5 with regeneration of silylium ion 2, which adds to the alkyne to construct the catalytic cycle (Scheme 3). Hence, the reaction using 1 and 1-hexyne (3c) was examined in a catalytic amount of TPFPB in benzene. Upon using 3c, the cyclization products **5ac** and **5bc** were obtained in 33% and 50% isolated yields, respectively (Scheme 4). This catalytic reaction is very interesting from the viewpoint of a transition metal-free reaction and a multistep catalytic reaction involving two types of carbocations with different reactivities.

In conclusion, we developed a dehydrogenative cyclization procedure using hydrosilanes and alkynes that is promoted by a transient silylium ion to give 1,2-dihydro-2-silanaphthalene derivatives. The regioselectivity of alkynes for the cyclization depended on the thermodynamic stability of the corresponding cations by resonance with the benzene ring, hyperconjugation of the alkyl group or the β -effect of another silyl group. 1,2,3,4-Tetrahydro-2-silanaphthalene derivatives were also successfully synthesized in the transition metal-free catalytic system containing cyclization and reduction steps.

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