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## COMMUNICATION

# Silylium Ion-promoted Dehydrogenative Cyclization: Synthesis of Silicon-containing Compounds Derived from Alkynes

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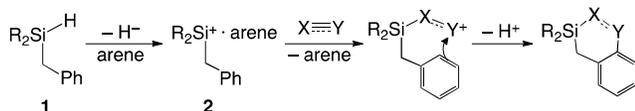
Received 00th January 2012,  
Accepted 00th January 2012Hidekazu Arie,<sup>a</sup> Takashi Kurihara,<sup>a</sup> Kunio Mochida<sup>\*a</sup> and Takayuki Kawashima<sup>\*b</sup>

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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-silapthalene 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 silylium ion<sup>1</sup> with a vacant p-orbital has an intrinsically high electrophilicity and can interact with  $\pi$ -donor nucleophiles such as alkenes, alkynes, and aromatic compounds, as well as ketones with a coordinative lone pair of electrons.<sup>2,3</sup> 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 a role of catalyst<sup>4-8</sup> as well as high reactive reagent.<sup>9</sup> The silylium ion, which is derived from treatment of the corresponding hydrosilane with trityl cation, exists usually as silane<sup>10</sup> or arene adducts<sup>2e</sup> and permits the transition metal-free consecutive hydrosilylation of unsaturated compounds.<sup>4</sup> Oestreich et al. have reported that the unique silylium ion bearing the ferrocenyl group undergoes a catalytic [4+2] cycloaddition with dienes or  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>6d</sup>



**Scheme 1** Strategy for silylium ion-promoted annulation using **1** and unsaturated compounds.

Recently, Müller and coworkers have successfully introduced carbon dioxide activated by the simple trialkylsilylium ion to an aromatic ring through electrophilic substitution.<sup>9a</sup> These facts prompted us to

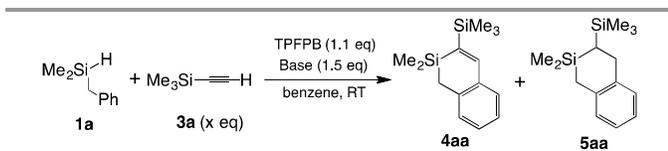
develop a silylium ion-promoted Friedel–Crafts reaction with unsaturated compounds, i.e., it was hypothesized that the  $\beta$ -silyl cations derived by the addition of silylium ions to the X–Y  $\pi$ -bonds, allow electrophilic substitution on the aromatic ring.

Kawashima et al. have synthesized dibenzosilole and trisilasumanene derivatives through the sila-Friedel–Crafts reaction, where the silylium ion forms a five-membered  $\pi$ -complex with an intramolecular aromatic moiety and consequent deprotonation from the  $\pi$ -complex with 2,6-lutidine produces the dibenzosilole derivatives.<sup>11</sup> Herein, we decided to use benzyldialkylsilanes ( $R_2BnSiH$ , **1**), in the case of which solvent-coordinated silylium ions [ $R_2BnSi\cdot arene$ ]<sup>†</sup> (**2**) interact with the appropriate unsaturated compounds to give the  $\beta$ -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-silapthalene derivative (**4aa**) except for entry 3 affording a mixture with **4aa** and 1,2,3,4-tetrahydro-2-silapthalene **5aa** (Scheme 1, Method A shown in ESI in detail). Among examined bases (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 proton sponge relative to DTBMP were less effective for the dehydrogenative cyclization because they may coordinate to the resulting silylium ion

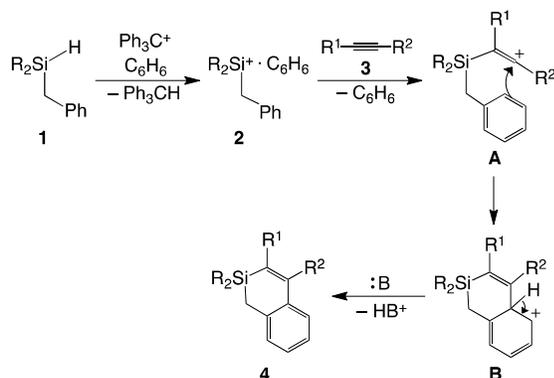
**2a** to interrupt the addition of alkyne.<sup>12</sup> In entry 3, use of Cs<sub>2</sub>CO<sub>3</sub> resulted in the formation of a mixture of **4aa** and **5aa**. As a result of optimizing the reaction conditions, the isolated yield of **4aa** was increased up to 73% upon addition of **1a** to the benzene solution of TFPFB, DTBMP, and **3a** (Method B) (entry 5).

**Table 1** Optimization of dehydrogenative cyclization using hydrosilane **1a** and trimethylsilylacetylene (**3a**)



Entry	Method	x eq	Base <sup>a</sup>	Product Yield (%) <sup>b</sup>	
				<b>4aa</b>	<b>5aa</b>
1	A	1.5	2,6-Lut	3	— <sup>c</sup>
2	A	1.5	proton sponge	6	— <sup>c</sup>
3	A	1.5	Cs <sub>2</sub> CO <sub>3</sub>	12	12
4	A	1.5	DTBMP	58	— <sup>c</sup>
5	B	3	DTBMP	73	— <sup>c</sup>

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



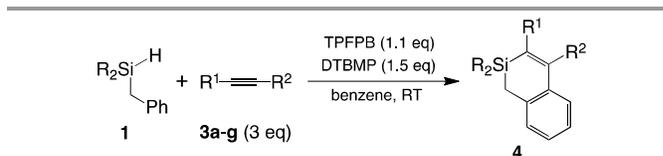
**Scheme 2** Plausible mechanism for the formation of **4** from hydrosilane **1** and alkynes **3**.

Compound **5aa** is considered to form by hydride abstraction of the protonated **4aa** from the Si–H bond of **1a**. Silylium ion-promoted catalytic hydrosilylation of various unsaturated compounds such as alkenes, alkynes, ketones, and imines has been reported,<sup>4</sup> and it is thought that the unsaturated compound activated by addition of the silylium ion abstracts the hydride from the hydrosilane to afford the hydrosilylation product and regenerates the silylium ion. Therefore, the above formation mechanism for **5aa** seems 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 sequent 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 (the β-effect of a silyl group). However, the cationic oligomerization of alkyne with the ethenyl cation **A** was not

completely prohibited under each of conditions, which caused a decrease in the yields of sila-cycle **4aa**.

Using the optimized Method B, the scope of hydrosilanes **1** and alkynes **3** is examined and the results are summarized in Table 2.<sup>13</sup> The cyclization using hydrosilane **1a** and phenylacetylene (**3b**) or 1-hexyne (**3c**) except for trimethylsilylacetylene (**3a**) as a terminal

**Table 2** Dehydrogenative cyclization using hydrosilanes **1a,b** with alkynes **3a-g**<sup>a</sup>

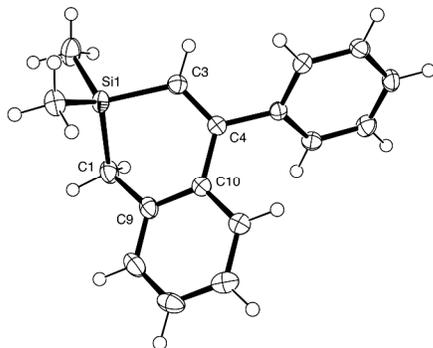


Entry	Silane <b>1</b>		Alkyne <b>3</b>		Product Yield (%) <sup>b</sup>
	R	R <sup>1</sup>	R <sup>2</sup>		
1	Me ( <b>1a</b> )	SiMe <sub>3</sub>	H	( <b>3a</b> )	73 ( <b>4aa</b> )
2	Me ( <b>1a</b> )	H	Ph	( <b>3b</b> )	34 ( <b>4ab</b> )
3	Me ( <b>1a</b> )	H	<sup>n</sup> Bu	( <b>3c</b> )	38 ( <b>4ac</b> )
4	Me ( <b>1a</b> )	H	<sup>t</sup> Bu	( <b>3d</b> )	— <sup>c</sup>
5	Me ( <b>1a</b> )	Ph	Ph	( <b>3e</b> )	77 ( <b>4ae</b> )
6	Me ( <b>1a</b> )	Et	Et	( <b>3f</b> )	34 <sup>d</sup> ( <b>4af</b> )
7	Me ( <b>1a</b> )	SiMe <sub>3</sub>	Ph	( <b>3g</b> )	— <sup>c</sup>
8	<sup>i</sup> Pr ( <b>1b</b> )	SiMe <sub>3</sub>	H	( <b>3a</b> )	71 ( <b>4ba</b> )
9	<sup>i</sup> Pr ( <b>1b</b> )	H	Ph	( <b>3b</b> )	67 ( <b>4bb</b> )
10	<sup>i</sup> Pr ( <b>1b</b> )	H	<sup>n</sup> Bu	( <b>3c</b> )	66 ( <b>4bc</b> )
11	<sup>i</sup> Pr ( <b>1b</b> )	Ph	Ph	( <b>3e</b> )	82 ( <b>4be</b> )
12	<sup>i</sup> Pr ( <b>1b</b> )	Et	Et	( <b>3f</b> )	39 <sup>d</sup> ( <b>4bf</b> )

<sup>a</sup> Using Method B. <sup>b</sup> Isolated yields based on **1**. <sup>c</sup> Complex mixture. <sup>d</sup> Using Method A. <sup>e</sup> Benzyldimethyl(2-phenylethynyl)silane (**6ag**) was obtained in 54% yield.

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 silyl groups at the β-position can be isolated and are stable even in benzene.<sup>14</sup> The remarkable stability of the isolated ethenyl cations seem 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 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-2-silanaphthalene backbone (Fig. S1). The good yield for the annulation of sterically bulky

diphenylacetylene is attributed to a prohibition of alkyne oligomerization by the resulting 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 desilylation reaction to give **6ag**.

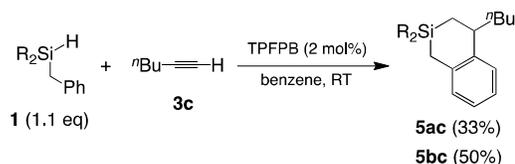


**Fig. 1** Crystal structure of one of the two independent molecules in **4ab**, showing 50% probability thermal ellipsoids.

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 the longer reaction time (30 min) than that using **1a** (15 min). The product yield for the reaction of **1b** with **3b** or **3c** was improved compared with those of **1a**, which can be understood by Thorpe-Ingold effect.<sup>15</sup> 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 in the viewpoint of a reduction of wastes. Considering the

forementioned formation mechanism of **5aa** shown 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, the carbocation **C** formed by the H-migration and aromatization from cyclohexadienyl cation **B**<sup>16</sup> 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 the 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 in viewpoints of a transition metal free reaction and a multistep catalytic reaction involving two types of carbocations with a different reactivity.



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

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  $\beta$ -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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## Notes and references

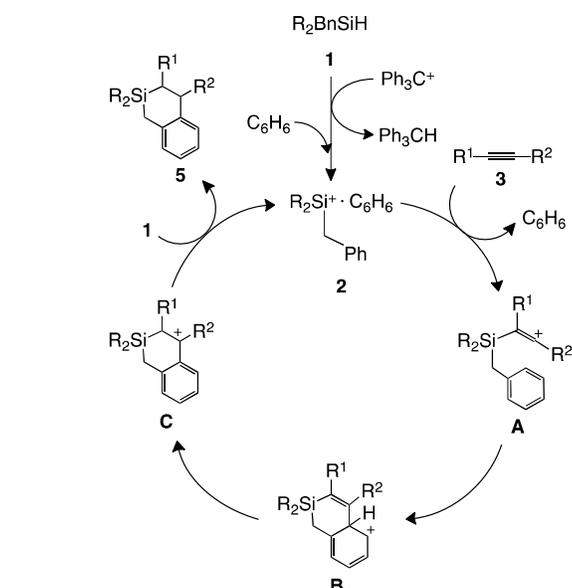
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† This work is dedicated to Professor Renji Okazaki on the occasion of his 77th birthday.

‡ Electronic Supplementary Information (ESI) available: Experimental section, the spectroscopic data and crystallographic data. CCDC 989789 for **4ab** and 989790 for **4ae**. See DOI: 10.1039/c000000x/

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

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- 16 Alternative path, in which arenes or alkyne work as a proton acceptor to convert cyclohexadienyl cation **B** to silacycle **4** that is protonated with the protonated arenes or alkyne to give carbocation **C**, cannot be ruled out absolutely.