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Special Issue

Metal-Free Carbocyclization of Homoallylic Silyl Ethers Leading to Cyclopropanes and Cyclobutanes

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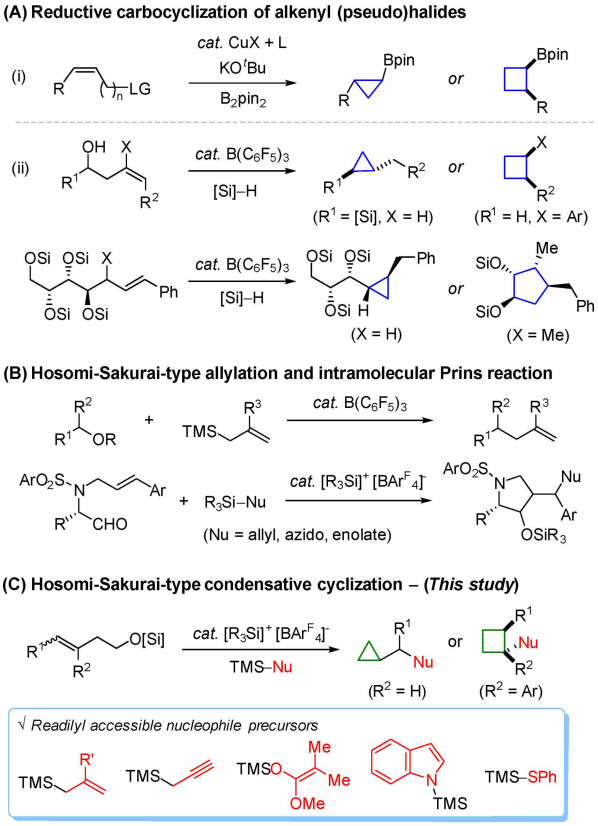
Abstract: We have developed a Hosomi-Sakurai type carbocyclization of homoallylic silyl ethers in reaction with silyl nucleophiles, catalyzed by Lewis acidic silylium salt. It offers cyclopropane and cyclobutane products with high efficiency and selectivity. A range of silyl nucleophiles could be engaged in this transformation to give small-sized carbocycles incorporating allyl, allenyl, carbonyl, indole or thioether groups. Diastereoselectivity in the cyclobutane formation was observed to be dependent on the steric bulkiness of incoming nucleophiles.

Small-sized carbocycles such as cyclopropanes and cyclobutanes are highly valuable intermediates in synthetic chemistry as they can undergo a range of subsequent transformations including C–C bond cleavage.[1] This carbocyclic motif is present in numerous natural compounds, and its structural features such as high ring-strain and/or rigidity often affect the resulting biological activities.[2] On the other hand, these distinguished characteristics may also cause obstacles in their construction. Catalytic preparative routes to cyclopropanes and cyclobutanes have been well established. For example, [2+2] cycloaddition between two alkenyl moieties is frequently utilized to obtain four-membered carbocycles with high stereoselectivity,[3] while cyclopropanes are readily accessible via carbene transfer to alkenes.[4]

As an alternative approach, reductive carbocyclization of alkenyl (pseudo)halides has been known.[5,6] Notably, Ito developed an elegant system consisted of copper catalyst and bis(pinacolato)diboron (B_2pin_2) for the reductive cyclization of alkenes bearing a leaving group (LG).[6] This reaction furnishes 3~5 membered borylated carbocycles with high diastereoselectivity [Scheme 1A(i)].

We recently demonstrated that Lewis acidic borane catalyst enables a condensative cyclization of homoallylic alcohols in reaction with hydrosilanes to provide disubstituted cyclopropanes and cyclobutanes with excellent selectivity.[7] An elegant example of $B(C_6F_5)_3$-catalyzed chemodivergent carbocyclization was revealed by Gagné, where unsaturated polyols are selectively transformed to cyclopropanes and cyclopentanes [Scheme 1A(ii)].[8] Notably, the chemoselectivity observed in the borane catalysis was highly dependent in the presence of substituents in the substrate skeleton (e.g. X = H *vs* Ar).

On the other hand, Gevorgyan reported the $B(C_6F_5)_3$-catalyzed Hosomi-Sakurai-type reductive allylation of benzylic or propargylic alcohol derivatives with allylsilanes.[9] Gagné also showed that a silylium ion can serve as a Lewis acid catalyst to promote an intramolecular Prins reaction with silyl nucleophiles (e.g. Nu = allyl, azido, or enolate) to afford functionalized pyrrolidines (Scheme 1B).[10] Based on these precedents, we envisioned that various functional groups can be installed during the course of a presupposed condensative cyclopropanation and cyclobutanation reactions under the Hosomi-Sakurai-type reaction conditions (Scheme 1C).[11] Described herein is the development of a silylium ion-initiated carbocyclization of homoallylic silyl ethers in reaction with silyl nucleo-



Scheme 1. Catalytic synthesis of cyclopropanes and cyclobutanes.

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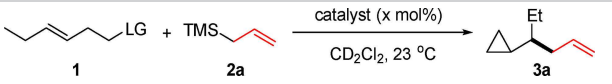
philes to afford functionalized cyclopropanes and cyclobutanes. The present metal-free catalysis operates efficiently under mild conditions.

At the outset of this study, we attempted to optimize reaction conditions by using homoallylic alcohol derivatives (**1**) in reaction with allylsilane (**2a**, 1.0 equiv) with the assistance of various types of Lewis acids (Table 1). In the presence of the Lambert salt $[Et_3Si][BAr^F_4]$ (Ar^F = pentafluorophenyl) as a catalyst (5 mol%), a series of leaving groups of substrate (**1**) was first examined. While no cyclization was observed in a reaction of free alcohol (LG = OH) with **2a** (entry 1), reactions of homoallylic alcohols masked by sulfonyl (LG = OMs, OTs), carbonate (OCO_2Ph) or silyl (OTMS, OTES) groups led to the formation of the desired cyclopropane **3a** in moderate to good yields (entries 2–6). Subsequently, an additional array of Lewis acids was screened by using **1a** (LG = OTMS) as a model substrate. When Et_3SiH (6 mol%) was added into a reaction solution containing a trityl salt $[Ph_3C][BAr^F_4]$ (5 mol%) in CD_2Cl_2 to generate Lambert salt *in situ* according to the literature,[10,12] the desired product **3a** was obtained in high yield (entry 7). Interestingly, when the trityl salt was employed alone instead of the Lambert salt, a similar level of reaction efficiency was observed (entry 8). On the other hand, $B(C_6F_5)_3$ rendered the reaction sluggish to furnish **3a** in 39% yield (entry 9), and BF_3 was decomposed presumably via a defluorination pathway in the presence of allylsilane (entry 10). No cyclization proceeded in the absence of Lewis acids (entry 11). Whereas moderate product yield was observed with reduced catalyst loading (1 mol%, entry 12), product **3a** was formed in high yield by adding 1.2 equiv. of allylsilane (entry 13). It is noteworthy that the newly installed allyl group in product **3a** was remained intact during the silylium ion catalysis.

Table 1. Optimization of Lewis acid-initiated cyclopropanation of homoallylic silyl ethers (**1**) with allylsilane (**2a**).[a]



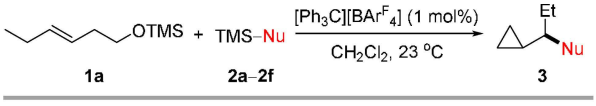
entry	catalyst [x mol%]	LG	t [h]	conv. [%][b]	yield [%][b]
1	$[Et_3Si][BAr^F_4]$ (5)	OH	12	7	<1
2	$[Et_3Si][BAr^F_4]$ (5)	OMs	0.5	99	54
3	$[Et_3Si][BAr^F_4]$ (5)	OTs	0.5	99	42
4	$[Et_3Si][BAr^F_4]$ (5)	OCO_2Ph	4	87	78
5	$[Et_3Si][BAr^F_4]$ (5)	OTMS	0.5	99	81
6	$[Et_3Si][BAr^F_4]$ (5)	OTES	0.5	99	63
7[c]	$[Ph_3C][BAr^F_4]$ (5)	OTMS	0.5	97	72
8	$[Ph_3C][BAr^F_4]$ (5)	OTMS	0.5	93	73
9	$B(C_6F_5)_3$ (5)	OTMS	12	45	39
10	$BF_3{\cdot}OEt_2$ (5)	OTMS	0.5	<1	<1
11	–	OTMS	12	<1	<1
12	$[Ph_3C][BAr^F_4]$ (1)	OTMS	0.5	78	60
13[d]	$[Ph_3C][BAr^F_4]$ (1)	OTMS	0.5	99	86

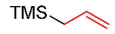
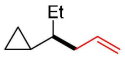
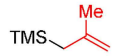
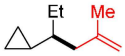
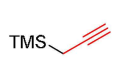
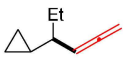
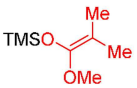
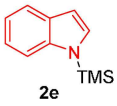
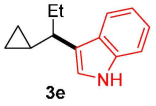
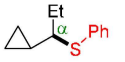
[a] Reaction conditions: **1** (0.2 mmol), **2a** (1.0 equiv), and catalyst (5 mol%) in CD_2Cl_2 (0.5 mL) at 23 °C for 0.5 ~ 12 h. [b] Determined by ^1H NMR analysis of the crude reaction mixture using an internal standard. [c] Et_3SiH (6 mol%) was added. [d] **2a** (1.2 equiv) was used. Ar^F = pentafluorophenyl, Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl, TMS = trimethylsilyl, and TES = triethylsilyl.

With the optimal conditions in hand (1 mol% of $[Ph_3C][BAr^F_4]$, 23 °C), a range of silyl nucleophiles (TMS-Nu, 1.2 equiv) was examined in the cyclopropanation of **1a** (Table 2). Not only parent allylsilane (**2a**), but also substituted reactant (**2b**) was readily reacted to afford the corresponding products (**3a** and **3b**) in good yields (entries 1 and 2). When propargylsilane (**2c**) was subjected to the above optimal conditions, an allene-substituted cyclopropane (**3c**) was obtained albeit in moderate yield (entry 3). Methyl trimethylsilyl dimethylketene acetal (**2d**) was readily reacted with **1a** to install a tertiary carbon at the α-position of cyclopropane product **3d** (entry 4). A reaction of **1a** with *N*-silyl-1*H*-indole (**2e**) also took place by the silylium ion catalysis to afford an indole product possessing a cyclopropyl moiety at the C3-position (entry 5). Notably, when a phenylthiosilane (**2f**) was employed as a nucleophile, a cyclopropyl thioether product (**3f**) was obtained in 71% yield along with a noncyclic bypoduct (14%) that was formed by a simple substitution of *O*-silyl group with thiolate (entry 6).

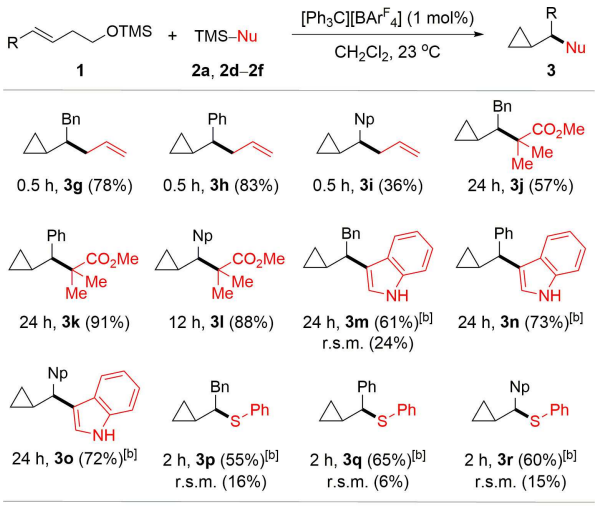
Encouraged by the above results, substrate scope (**1**) was next investigated in combination with additional silyl nucleophiles **2** (Scheme 2). Benzyl and phenyl substituents at the alkenyl moiety in substrates were found to be facile in the allylative cyclization with **2a** (1.2 equiv) in the presence of $[Ph_3C][BAr^F_4]$ (1 mol%) to give the corresponding cyclopropanes

Table 2. Scope of TMS–Nu in the cyclopropanation of **1a**[a].



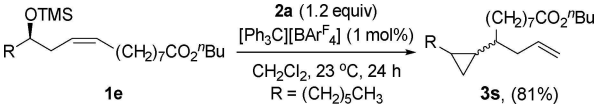
entry	TMS–Nu	t (h)	product	yield (%)[b]
1	 **2a**	0.5	 **3a**	86
2	 **2b**	0.5	 **3b**	72
3	 **2c**	12	 **3c**	45
4	 **2d**	0.5	 **3d**	90
5	 **2e**	24	 **3e**	(59)[c]
6	TMS–SPh **2f**	2	 **3f**	(71)[c,d]

[a] Reaction conditions: **1a** (0.2 mmol), **2a–2f** (1.2 equiv), and $[Ph_3C][BAr^F_4]$ (1 mol%) in CH_2Cl_2 (0.5 mL) at 23 °C for 0.5 ~ 24 h. [b] Determined by ^1H NMR analysis of the crude reaction mixture on the basis of an internal standard. [c] $[Ph_3C][BAr^F_4]$ (5 mol%) was used: isolated yield. [d] A linear byproduct, (*E*)-1-(phenylthio)hex-3-ene, was also isolated in 14%.



[a] Reaction conditions: **1** (0.4 mmol), **2** (1.2 equiv), and $[Ph_3C][BAr^F_4]$ (1 mol%) in CH_2Cl_2 (1.0 mL) at 23 °C for 0.5~24 h: isolated yields. [b] $[Ph_3C][BAr^F_4]$ (5 mol%) was used. Bn = benzyl, Np = 2-naphthyl, r.s.m. = recovery of starting material (**1**).

Scheme 2. Substrate scope in the functionalizative cyclopropanation.[a]



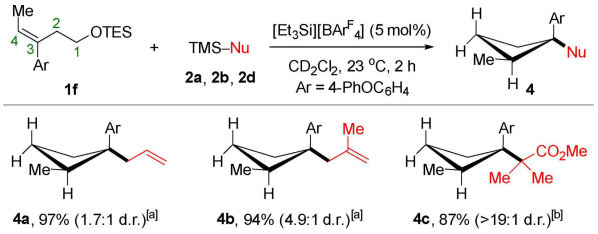
Scheme 3. Cyclopropanation of **1e** with allylsilane (**2a**).

in 78% and 83% yields at room temperature, respectively (**3g** and **3h**).

A cyclization of (2-naphthyl)-substituted homoallylic silyl ether with **2a** afforded **3i** in lower yield mainly due to side reactions at the naphthalene moiety.[13] Silyl ketene acetal (**2d**) was readily reacted with a range of homoallylic silyl ethers under the standard conditions to furnish the corresponding cyclopropane products in moderate to high yields (**3j**–**3l**). Considering the fact that indole derivatives are widely accessible via the C–H bond activation approach,[14] we wondered whether the current procedure can serve as a synthetic platform for those valuable compounds. When N-silyl indole (**2e**) was employed as a nucleophile for the carbocyclization of homoallylic silyl ethers, 1*H*-indole derivatives carrying cyclopropylmethyl substituents at the C3-position of indole were obtained in reasonable yields (**3m**–**3o**). Moreover, a phenylthio group could readily be incorporated into a product via the current silylium-catalyzed carbocyclization (**3p**–**3r**).

A cyclization of *O*-silyl ricinoleate ester (**1e**) with allylsilane (**2a**) took place smoothly to afford a mixture of diastereomeric products in good yield (Scheme 3). Again, it demonstrates that the present mild reaction conditions are compatible with labile functional groups.

We next endeavoured to further expand the scope of carbocyclization to include cyclobutanes. As described in Scheme 1A(ii), a borane-catalyzed divergent carbocyclization of alkenyl alcohols, which leads to cyclopropanes or cyclobutanes, has been disclosed relying on the electronic properties of substituents on the alkenyl moiety.[7a] The electronically rich aryl group at the C3-position plays a pivotal role in the selective cyclobutanation. Accordingly, we examined three types of TMS-Nu (**2a**, **2b**, and **2d**) for the supposed cyclobutanation of a homoallylic silyl ether bearing an aryl group at the C3-position (**1f**) (Scheme 4). To our delight, the reaction proceeded

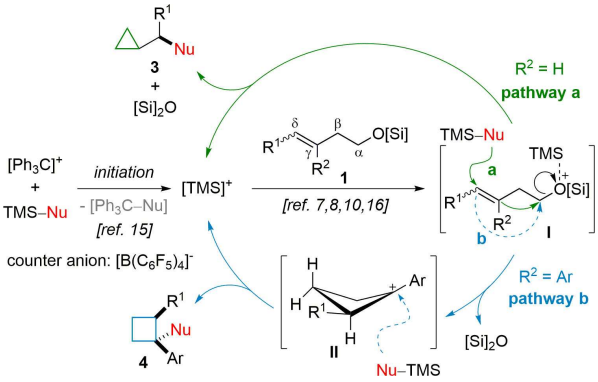


[a] Crude ^{1}H NMR yield based on internal standard. [b] 24 h, isolated yield.

Scheme 4. Catalytic synthesis of functionalized cyclobutanes.

smoothly to produce the desired functionalized cyclobutanes in high yields under the current silylium ion catalysis. Notably, diastereoselectivity in this carbocyclization was keenly dependent on the steric bulkiness of nucleophiles employed (**4a** and **4b**). When a sterically more demanding nucleophile (**2d**) was used, one of the diastereomers was formed almost exclusively (**4c**).

Based on the present results and precedent literature,[7–11] plausible carbocyclization pathways are depicted in Scheme 5. Firstly, trityl ion salt, a catalyst precursor, is believed to exchange its cation with silylium derived from silyl nucleophiles (TMS-Nu) to form $[Ph_3C$-Nu] and $[TMS]^+[BAr^F_4]^-$.[15] It is proposed that the substrate (**1**), homoallylic silyl ether, is activated by the *in situ* generated silylium by forming *O*-silyl oxonium species (**I**).[7,8,10,16] For disubstituted olefinic substrates (R^2 = H), this activated species **I** is assumed to react with a nucleophile at the vinylic δ-carbon to induce an intramolecular cyclization (S_N2') leading to a cyclopropane product (**3**) with the regeneration of silylium ion, accompanied by the release of siloxane (pathway a).[7b] When trisubstituted olefinic substrates (R^2 = Ar) are subjected, we propose a stepwise process (pathway b) involving an intramolecular ring closure of **I** to generate a benzylic cationic cyclobutane intermediate **II** that will subsequently



Scheme 5. Proposed pathways of the silylium-catalyzed carbocyclization.

reacts with TMS-Nu. Steric bias is assumed to direct this addition step, resulting in the observed diastereoselectivity.[7a]

In summary, we have developed a highly mild and metal-free carbocyclization of homoallylic silyl ethers to furnish cyclopropanes and cyclobutanes in reaction with silyl nucleophiles. The reaction is catalyzed by Lewis acidic silylium salt with high efficiency and selectivity, and it was compatible with various functional groups. This procedure was utilized in the carbocyclization of unsaturated fatty acid derivative to afford multiply substituted cyclopropanes.

Experimental Section

General procedure of cyclopropanation reactions: In a glove box, $[Ph_3C][BAr^F{}_4]$ (3.7 mg, 1 mol%) was dissolved in CH_2Cl_2 (1.0 mL) in a reaction vial, into which TMS-Nu (**2**, 1.2 equiv) and **1** (0.4 mmol, 1.0 equiv) were added and the mixture was stirred at 23 °C for 0.5 ~ 24 h. Upon the completion of the reaction, the mixture was quenched by adding Et_3N. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Silylium ion catalysis · Carbocyclization · Hosomi-Sakurai reaction · Cyclopropanes · Cyclobutanes

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