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COMMUNICATIONS

Metal-Catalyzed Silacyclopropanation of Mono- and Disubstituted Alkenes

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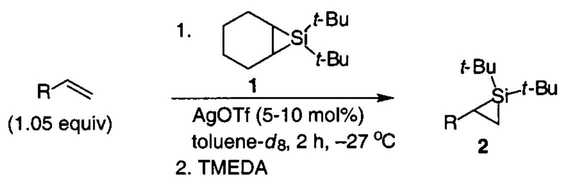
Silacyclopropanes are highly reactive compounds that undergo a number of stereoselective carbon−carbon bond-forming reactions.[1] The most general method for forming silacyclopropanes involves the reaction of an alkene with a free silylene or a silylenoid intermediate. The substrate compatibility of alkene silacyclopropanation, however, is limited because the generation of a silylene species requires the use of elevated temperatures, strongly reducing conditions, or photolysis.[2−4] To develop milder conditions for alkene silacyclopropanation, we hoped to employ a catalyst to generate and transfer silylenes.[5] While metal-catalyzed reactions are commonly employed for the synthesis of three-membered rings from alkenes,[6,7] the catalytic silacyclopropanation of alkenes is unknown. In this communication we report a metal-catalyzed silacyclopropanation of mono- and disubstituted alkenes that proceeds at −27 °C. This transformation allows for the one-step conversion of alkenes to oxasilacyclopentanes.

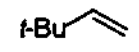
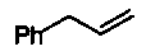
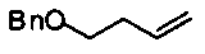
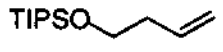
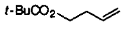
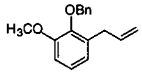
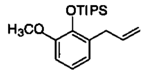
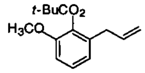
Since *t*-Bu_2Si can be generated thermally from silacyclopropane **1**,[2] we sought to promote this reaction at reduced temperatures through the use of a catalyst (eq 1). A survey of metal salts as possible promoters of silylene transfer was undertaken. Several salts reduced the temperature of silylene transfer to room temperature or below, including those of $CeCl_3$, $Cu(OTf)_2$, and $(CuOTf)_2$−benzene. The transfer could be promoted at temperatures as low as −27 °C with silver triflate as catalyst.[8]

Once silver triflate was identified as the most active catalyst, the effects of solvent, concentration, temperature, and catalyst loading were examined. A screen of solvents revealed that toluene and methylene chloride afforded the best yields and allowed the lowest temperatures for transfer. The yield of the transfer did not vary with concentrations between 0.1 and 0.5 M. As little as 1 mol % AgOTf effected complete silylene transfer in 2 h at −27 °C. Lower catalyst loadings required higher temperatures (room temperature) and increased reaction times.



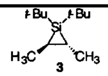
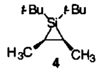
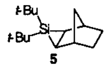
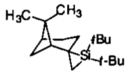
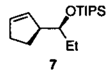
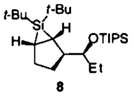
(1)

Table 1. Silacyclopropanation of Monosubstituted Alkenes (eq 1)

Entry	Alkene	% yield[a]
1		90
2[b]		99
3		96
4		90
5		71
6		82
7		67
8		61
9		72
10		83

[a] As determined by ^1H NMR spectroscopic analysis of the product mixture relative to an internal $PhSi(CH_3)_3$ standard. [b] An excess (ca. 5 equiv) of alkene was used.

Table 2. Silacyclopropanation of Disubstituted Olefins

Entry	Alkene	Product	% yield[a]
1	*trans*-butene[b]	 **3**	99
2	*cis*-butene[b]	 **4**	92
3	norbornylene	 **5**	90[c]
4	β-pinene	 **6**	72[c]
5	 **7**	 **8**	85[c]

[a] As determined by ^1H NMR spectroscopic analysis of product mixture relative to an internal standard of $PhSi(CH_3)_3$ or 1,3 dimethoxybenzene. [b] An excess of alkene was used. [c] One diastereomer visible by ^1H and ^{29}Si NMR spectroscopy (dr ≥95:5).

A variety of silacyclopropanes were formed from monosubstituted alkenes using the silver triflate-catalyzed conditions (eq 1, Table 1).[8] Because of their increased sensitivity under the reaction conditions, the silacyclopropanes were not isolated.[9] The transfer of the silylenoid species was not affected by the size of the alkene substituent (entries 1−3). The functional group tolerance of the silver triflate-catalyzed silacyclopropanation is illustrated in entries 5−10. Aryl, benzyl, and silyl ethers are compatible with the reaction conditions, and even primary and aryl pivaloate esters (entries 7 and 10) afforded high yields of the corresponding silacyclopropanes.

In addition to silacyclopropanes **2**, a range of silacyclopropanes can be formed from disubstituted alkenes under the silver triflate conditions (Table 2). This reaction is stereospecific, since *trans*- and *cis*-2-butene (entries 1 and 2) afford solely the corresponding

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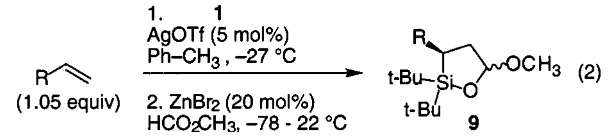
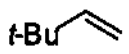
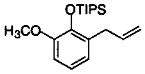


Table 3. One-Flask Silylene Transfer, Methyl Formate Insertion (eq 2)

Entry	Alkene	Regiosel.[a]	d.r.[a]	% Yield[b]
1		>99:1	76:24	87
2		>99:1	70:30	92
3		74:26	(major) 55:45 (minor) 91:9	75
4		97:3	(major) 70:30	80
5		>99:1	64:36	61
6		96:4	70:30	61
7		>99:1	70:30	82

[a] As determined by ^{1}H NMR spectroscopic analysis of crude product mixture. [b] Isolated yield from alkene after purification by flash chromatography.

trans- and *cis*-dimethyl silacyclopropanes (**3** and **4**, respectively).[10] The silver-catalyzed silacyclopropanation was also found to be diastereoselective (entries 3–5). One product diastereomer was observed in good yield for norbornylene (entry 3). The silylenoid approaches from the more accessible *exo* face to provide **5**.[11] *β*-Pinene and the substituted cyclopentene **7** also reacted in a stereoselective manner to afford single diastereomers of **6** and **8** by ^{1}H and ^{29}Si NMR spectroscopy (entries 5 and 6). These selectivities represent an improvement in the diastereomeric ratios relative to those obtained under conditions for the thermal transfer of silylene.[11,12]

The catalyzed silacyclopropanation reaction could be used as part of a one-step procedure to convert alkenes into oxasilacyclopentanes without isolation of air-sensitive silacyclopropane intermediates. Silver triflate-catalyzed silacyclopropanation of monosubstituted alkenes was followed by zinc bromide-catalyzed insertion of methyl formate into the carbon–silicon bond of the silacyclopropane intermediate to afford the products **9** (eq 2, Table 3**)**.[13,14] High yields were observed over the two-step sequence with the butyl-, isopropyl-, and benzyl-substituted alkenes (entries 1, 2, and 4). While the silylene-transfer reaction was not affected by the steric bulk of alkene, the regioselectivity of the formate insertion decreased with the large *tert*-butyl substituent on the silacyclopropane (entry 3).[13] The second insertion step of the reaction sequence was less functional group tolerant than the silylene transfer, but good yields were observed with primary benzyl and silyl ethers (entries 5 and 6). Aryl silyl ethers (entry 7) were also tolerated in this reaction.

Silver triflate-catalyzed di-*tert*-butyl silylene transfer from silacyclopropane **1** to functionalized alkenes followed by in situ ring expansion with methyl formate provides an efficient one-flask synthesis of functionalized oxasilacyclopentanes from alkenes. The low temperature and short reaction time for silylene transfer result in an improvement in diastereoselectivity and substrate compatibility as compared to previous methods used to form silacyclopropanes.[2–4,11] The product oxasilacyclopentanes have been previously shown to undergo stereoselective carbon–carbon bond-forming reactions through formation of an oxocarbenium ion and trapping with the appropriate nucleophile.[1,15] The catalytic silver triflate conditions greatly enhance the synthetic utility of silacyclopropanation by increasing the availability of functionalized silacyclopropanes.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) For recent examples refer to: (a) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534–540. (b) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702–9703. (c) Sharma, H. K.; Pannell, K. H. *Organometallics* **2001**, *20*, 7–9. (d) Tobita, H.; Sato, T.; Okazaki, M.; Ogino, H. *J. Organomet. Chem.* **2000**, *611*, 314–322. (e) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599–5601.
(6) For recent examples refer to: (a) Boche, G.; Lohrenz, J. C. W. *Chem. Rev.* **2001**, *101*, 697–756. (b) (aziridination) Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707–7708. (c) (epoxidation) Daly, A. M.; Renehan, M. F.; Gilheany, D. G. *Org. Lett.* **2001**, *3*, 663–666. (d) (cyclopropanation) Davies, H. M. L.; Panaro, S. A. *Tetrahedron* **2000**, *56*, 4871–4880.
(7) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824–4827.
(8) To screen lower reaction temperatures, TMEDA was added to sequester the metal and prevent further reaction so analysis by ^{1}H NMR spectroscopy of the reaction mixtures could be performed at ambient temperature.
(9) The silver triflate-catalyzed silacyclopropanation reaction was monitored by ^{1}H and ^{29}Si NMR spectroscopy with an internal standard of PhSi(CH$_3$)$_3$. Refer to Supporting Information for more details.
(10) The identification of the products was determined by correlation with previously prepared *cis*- and *trans*-dimethyl silacyclopropane.
(11) Driver, T. G.; Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6524–6525.
(12) The thermolysis of silacyclopropane **1** in the presence of *β*-pinene and cyclopentene **7** provided silacyclopropanes **6** and **8** as 70:30 and 94:6 mixtures of diastereomers.
(13) Franz, A. K.; Woerpel, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4295–4299.
(14) **Representative Method for the One-Flask Construction of Oxasilacyclopentanes from Monosubstituted Alkenes:** To a cooled, heterogeneous solution (−27 °C) of AgOTf (0.010 g, 0.039 mmol) in 2 mL of toluene was added 1-hexene (0.125 mL, 0.996 mmol) followed by the dropwise addition of a solution of **1** (0.210 g, 0.936 mmol) in 1 mL of toluene. After 2 h the black solution was cooled to −78 °C, and methyl formate (0.175 mL, 2.83 mmol) and ZnBr$_2$ (0.034 g, 0.15 mmol) were added. The heterogeneous mixture was allowed to warm to 25 °C over 16 h. After addition of 10 mL of H$_2$O, the mixture was extracted with 3 × 5 mL of Et$_2$O. The combined organic phases were washed with 10 mL of NaHCO$_3$ (saturated aqueous) and 10 mL of brine. The resulting organic phase was dried (MgSO$_4$), filtered, and concentrated in vacuo to afford the oxasilacyclopentane **9** as a 76:24 mixture of diastereomers by ^{1}H NMR spectroscopy. Purification by flash chromatography (3:97 Et$_2$O:hexanes) provided the product as a clear oil (0.232 g, 87%).
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