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Acid-catalyzed cyclization of vinylsilanes bearing a hydroxy group. Benzyldimethylsilyl group as an effective promoter and novel hydroxy surrogate[1]

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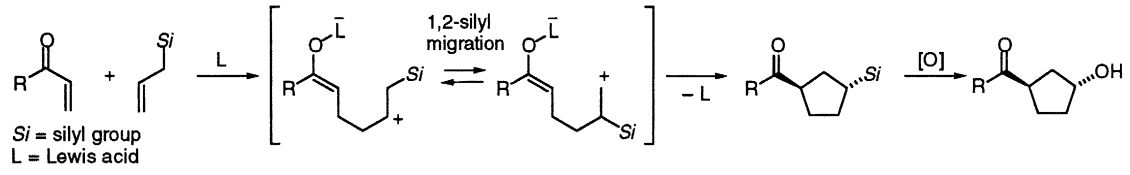
Abstract

A benzyldimethylsilyl (BnDMS) group was found to effectively enhance the reactivity of vinylsilanes toward the acid-catalyzed intramolecular addition of a hydroxy group in comparison with a dimethylphenylsilyl group. The BnDMS group of the resultant cyclized products could be easily converted to a hydroxy group by the action of TBAF–H_2O_2–$KHCO_3$. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: cyclization; acid catalyst; silicon and compound; oxidation.

It is well recognized that electrophilic substitution of allylsilanes and vinylsilanes proceeds via β-silylcarbenium ion intermediates due to the directing effect of a silyl group.[2] In recent years, much attention has been paid to carbon–carbon and carbon–hetero atom bond formation by intramolecular nucleophilic trap of the intermediates because it provides a powerful tool for the stereoselective construction of carbocycles and heterocycles as proved in the Lewis acid-mediated [3+2] cycloaddition of allylsilanes (Eq. (1)).[3] In this process, the silyl group of the employed silicon reagent remains in the cyclized product. Therefore, from the viewpoint of synthetic utility, the silyl group should be not only effective in promoting this process but also easily convertible to a hydroxy group by oxidative cleavage of the Si–C bond.[4] Studies on the [3+2] cycloaddition of allylsilanes from this aspect have revealed that some bulky silyl groups meet these requirements.[5]



(1)

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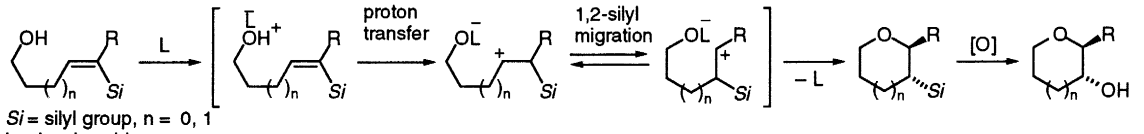
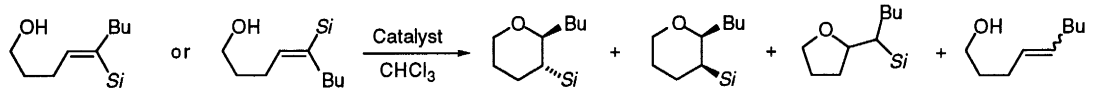
Previously, we have reported that the acid-catalyzed 1,2-silyl migrative cyclization of vinylsilanes bearing a hydroxy group is valuable in the stereoselective synthesis of certain cyclic ethers (Eq. (2)).[6] A dimethylphenylsilyl (DMPS) group is usable for this cyclization via a β-silylcarbenium ion intermediate, and the resultant product can be transformed to the corresponding alcohol by the known two-step procedure.[7] However, the efficiency of cyclization is not so high. While a *t*-butyldimethylsilyl (TBDMS) group effectively promotes the cyclization, it cannot be converted to a hydroxy group. We herein report that a benzyldimethylsilyl (BnDMS) group imparts high reactivity toward the cyclization to vinylsilanes like the TBDMS group and serves as an efficient latent hydroxy group.



(2)

As reported previously,[6] treatment of vinylsilane (*Z*)-**1b** with $TiCl_4$ for 9.5 h afforded only *trans*-**2b** in 75% yield (Eq. (3)). In the present study, we initially found that the cyclization of (*Z*)-**1a** was completed in 1.5 h, forming **2a** in a comparable yield with reduced *trans*-selectivity (Eq. (3) and entry 1 in Table 1). Thus, the BnDMS group considerably accelerated the cyclization. The use of $TiCl_2(O\text{-}i\text{-}Pr)_2$ for (*Z*)-**1a** achieved a higher yield and *trans*-selectivity (entry 2) although the less Lewis acidic catalyst was not suitable for (*Z*)-**1b**. The cyclization of (*Z*)-**1a** proceeded even at 0°C and exhibited still higher selectivity (entry 3). AcCl also worked as an efficient catalyst for (*Z*)-**1a** (entry 4).[8] Interestingly, in this case, a certain formation of **3a** was observed.[9] Similar to the result with (*E*)-**1b**,[6] the reaction of (*E*)-**1a** gave disappointing results in both yield and stereoselectivity (entry 5).



(3)

Table 1
Acid-catalyzed cyclization of vinylsilanes **1a**[a]

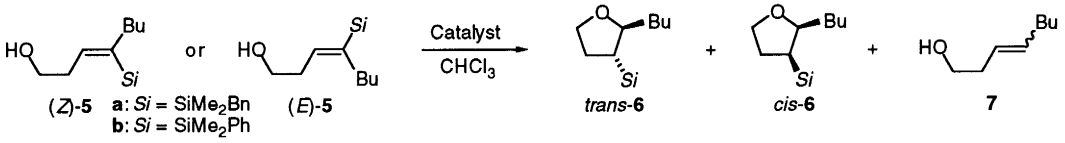
Entry	Substrate	Catalyst	Temp	Time / h	**2a**[b]		**3a**[b]	**4**	**1a**
					Y. / %	*trans* : *cis*	Y. / %	Y. / %	Y. / %
1	(*Z*)-**1a**	$TiCl_4$	rt	1.5	78	95 : 5	1	17	4
2		$TiCl_2(O\text{-}i\text{-}Pr)_2$	rt	13	91	97 : 3	1	-	-
3		$TiCl_2(O\text{-}i\text{-}Pr)_2$	0 °C	40	89	99 : 1	3	-	-
4		AcCl	rt	9	82	99 : 1	13	-	-
5	(*E*)-**1a**[c]	$TiCl_4$	rt	26	31	36 : 64	<1	31	22

[a] Conditions: vinylsilane (0.50 mmol), catalyst (0.025 mmol), and $CHCl_3$ (2.5 mL). [b] The products **2a** and **3a** were obtained as a mixture. The yields and isomeric ratio were determined by GC analysis. [c] *E*:*Z* = 97:3.

Judging from the previous and present results,[6] the ability of a BnDMS group to accelerate the 1,2-silyl-migrative cyclization exceeds those of DMPS and TMS groups, but it is not as high as that of a TBDMS group. The low ability of the DMPS group is probably due to the electron-withdrawing character of the phenyl group,[10] which would decelerate the rate-determining proton transfer to the sp^2 carbon α to the silyl group (Eq. (2)).[6] In the case with the TMS group, desilylation of the substrate to **4** becomes a

serious problem. The side reaction also diminishes the accelerating ability of the BnDMS group to some extent.

The cyclization of (*Z*)- and (*E*)-vinylsilanes **5a** were also examined (Eq. (4) and Table 2). In both systems using $TiCl_4$ and TsOH, (*Z*)-**5a** was smoothly cyclized to *trans*-**6a** unlike (*Z*)-**5b**.[6] In addition, the use of (*E*)-**5a** provided *cis*-**6a** in a reasonable yield with high stereoselectivity.[11]



(*Z*)-**5** **a**: *Si* = $SiMe_2Bn$ (*E*)-**5** **b**: *Si* = $SiMe_2Ph$ *trans*-**6** *cis*-**6** **7**

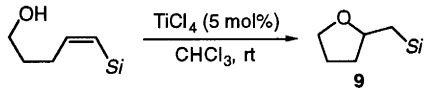
(4)

Table 2
Acid-catalyzed cyclization of vinylsilanes **5a**[a]

Substrate	Catalyst	Temp / °C	Time / h	**6a**		**7**	**5a**
				Y. / %	*trans* : *cis*[b]	Y. / %	Y. / %
(*Z*)-**5a**	$TiCl_4$	rt	13	90	99 : 1	-	-
	TsOH	60	19	91	99 : 1	-	-
(*E*)-**5a**	TsOH	60	13	66	2 : 98	13	14

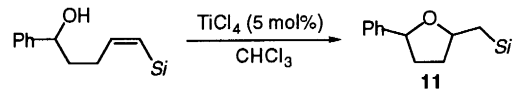
[a]See footnote a in Table 1. [b]Determined by GC analysis.

Vinylsilanes **8** and **10** bearing no α-substituent underwent the cyclization without 1,2-silyl migration to turn to 2-(silylmethyl)tetrahydrofurans **9** and **11**, respectively, in accordance with the cyclization of their DMPS analogues (Eqs. (5) and (6)).[12] In this case also, the BnDMS group was more effective in accelerating the cyclization than the DMPS group. The $TiCl_4$-catalyzed cyclization of **10** resulted in a slightly lower diastereoselectivity than that of its DMPS analogue at rt. However, the high reactivity of **10** enabled the cyclization at −20°C, which effected high *trans*-selectivity.



(*Z*)-**8**: *Si* = $SiMe_2Bn$ 0.75 h **9** 96%

(5)

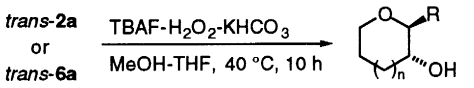


(*Z*)-**10**: *Si* = $SiMe_2Bn$ **11**

rt, 0.67 h 89% (*trans:cis* = 88:12)
-20 °C, 23 h 86% (*trans:cis* = 95:5)

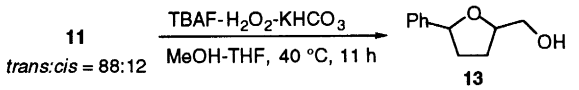
(6)

We have already shown that the DMPS group of *trans*-**2b** or *trans*-**6b** can be converted to a hydroxy group by treatment with *t*-BuOK/DMSO followed by TBAF–H_2O_2–$KHCO_3$/MeOH–THF (**12a** from *trans*-**2b**, 88%; **12b** from *trans*-**6b**, 89%).[6,7] In the present study, it turned out that the cyclized products bearing a BnDMS group were smoothly oxidized to the corresponding alcohols in one-step using only the latter set of reagents (Eqs. (7) and (8)). The yields of alcohols **12** from *trans*-**2a** and *trans*-**6a** were comparable to those from *trans*-**2b** and *trans*-**6b**. The oxidation of **11** gave a much better result than that of its DMPS analogue (59% by the two-step procedure).



12a: n = 1, 82%
12b: n = 0, 87%

(7)



13
92%, *trans:cis* = 88:12

(8)

In conclusion, we have succeeded in enhancing the synthetic utility of the acid-catalyzed cyclization of vinylsilanes by the introduction of a BnDMS group. The silyl group works as an effective promoter of the cyclization and a novel hydroxy surrogate. We are further studying the stereoselective synthesis of cyclic ethers utilizing the directing effect of the BnDMS group, and the results will be reported in due course.

Acknowledgements

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References

1. Studies on Organosilicon Chemistry. No. 149.
2. (a) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (b) Panek, J. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, p. 579. (c) Fleming, I.; Dunoguès, J.; Smithers, R. H. *Org. React.* **1989**, *37*, 57. (d) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Ed.; Wiley: Chichester, 1989; Part 2, p. 893. (e) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (f) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.
3. (a) Knölker, H.-J. *J. Prakt. Chem.* **1997**, *339*, 304. (b) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293.
4. (a) Colvin, E. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 7, p. 641. (b) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.
5. (a) Akiyama, T.; Hoshi, E.; Fujiyoshi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2121. (b) Groaning, M. D.; Brengel, G. P.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 5517. (c) Knölker, H.-J.; Jones, P. G.; Wanzl, G. *Synlett* **1998**, 613. (d) Suginome, M.; Matsunaga, S.; Ito, Y. *Synlett* **1995**, 941.
6. Miura, K.; Hondo, T.; Saito, H.; Ito, H.; Hosomi, A. *J. Org. Chem.* **1997**, *62*, 8292.
7. (a) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C 37.
8. The actual catalyst would be HCl generated by the reaction of the hydroxy group of the substrate with AcCl. See Ref. 6.
9. The cyclized product **3a** can be isomerized to **2a** by the action of $TiCl_4$. The AcCl-catalyzed cyclization of **1a** followed by a brief treatment (10 min) with 5 mol$TiCl_4$ gave **2a** in 89% (*trans:cis*=98:2) along with less than 1% of **3a**.
10. Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938.
11. The reason for the stereospecific cyclization can be explained by the reaction mechanism previously proposed by us. See Ref. 6.
12. (a) Miura, K.; Okajima, S.; Hondo, T.; Hosomi, A. *Tetrahedron Lett.* **1995**, *36*, 1483. (b) Miura, K.; Hondo, T.; Okajima, S.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 487.