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Acid-Catalyzed Rearrangement of α-Hydroxycyclopropylsilanes

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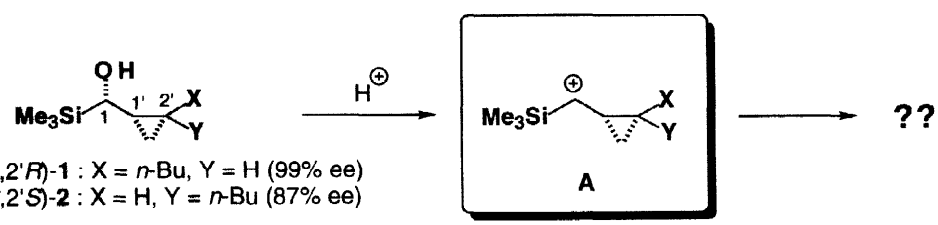
Abstract

Acidic treatment of the (1*S*,1'*S*,2'*R*)-α-hydroxycyclopropylsilane **1** gave a mixture of rearranged products, which were composed of the ring-opened (*S*)-vinylsilane **3**, the tandem [1,2]-CC bond migration product (1*S*,2*R*,1'*S*)-silylcyclopropane **4**, and its 1'*R* isomer **5**, respectively. Hence, the use of the 2'*S* isomer **2** produced a mixture of the (*R*)-**3**, **4**, and **5**. Our proposed mechanisms of the present cationic rearrangement are also described.

Keywords: acid-catalyzed rearrangement; α-hydroxycyclopropylsilane; cyclobutyl cation; [1,2]-CC bond migration

In the preceding paper, we described the chiral α-hydroxysilyl group to be an excellent chirality transferring group as well as a masked form convertible to a carboxylic acid, which was demonstrated by their successful conversion into the optically active 2-substituted-cyclopropanecarboxylic acids via the (1*S*,1'*S*,2'*R*)-α-hydroxycyclopropylsilane **1** and its 2'*S* isomer **2**. [1] Our further interest in the α-hydroxycyclopropylsilanes led us to examine the mode of their cationic rearrangement, since the hydroxyl group of **1** and **2** lies on both the cyclopropylcarbinyl position and α-position of the trimethylsilyl (TMS) group. The purpose of the present paper is to describe the fate of the hitherto unprecedented α-silyl cation **A**. [2,3]



(1*S*,1'*S*,2'*R*)-**1** : X = *n*-Bu, Y = H (99% ee)
(1*S*,1'*S*,2'*S*)-**2** : X = H, Y = *n*-Bu (87% ee)

Our initial attempt to generate the cationic species was the treatment of optically active **1** (99% ee) [1] with 10% H_2SO_4 (2 equiv) in tetrahydrofuran (THF). Upon standing the solution at room temperature, the starting **1** was completely consumed within 4 h to give a mixture of products which were composed of mainly three products **3a** - **5a**. [4] ^{1}H NMR spectrum of the mixture suggested the presence of a vinyl group in **3a** and a cyclopropyl group in both **4a** and **5a**. Pure **5a** was isolated from the mixture by column chromatography on silica gel (*n*-hexane/AcOEt = 30/1(v/v)) and the remaining mixture (**3a** and **4a**) was separated by $AgNO_3$ pre-coated TLC. [5] ^{1}H and ^{13}C NMR data and extensive COSY and NOESY experiments of

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each product suggested that the structures of **3a** - **5a** were (*E*)-4-hydroxy-1-trimethylsilyl-oct-1-ene (**3a**, Julia-type rearranged product [6]), 1-(1'-hydroxy)pentyl-2-trimethylsilylcyclopropane (**4a**), and its 1'-hydroxy diastereomer (**5a**), respectively (Scheme 1, Table). [7] The relative configuration between the hydroxy group and the cyclopropane ring in **5a** was determined to be as depicted by an alternative synthesis of racemic **5a**. [8] Therefore, the relative stereochemistry of **4a** was unambiguously assigned as the diastereomer of **5a** at the hydroxy position. It was of particular interest to examine whether the products were obtained in optically active form. This was easily ascertained by converting **3a** - **5a** to the corresponding MTPA esters, respectively. [9] Since each (*R*)-MTPA ester was obtained as a single diastereomer, it was found that the optical purity of starting **1** was completely retained in the products (99% ee). Furthermore, the ^{1}H NMR comparisons of the (*R*)-MTPA ester of each product with the corresponding (*S*)-MTPA ester (modified Mosher's method) [10] assigned the absolute structures of **3a** - **5a** to be (*S*)-**3a**, (1*S*,2*R*,1'*S*)-**4a**, and (1*S*,2*R*,1'*R*)-**5a**, respectively. [11] Thus, the absolute structures of the three solvolysis products were confirmed. [12]

Scheme 1

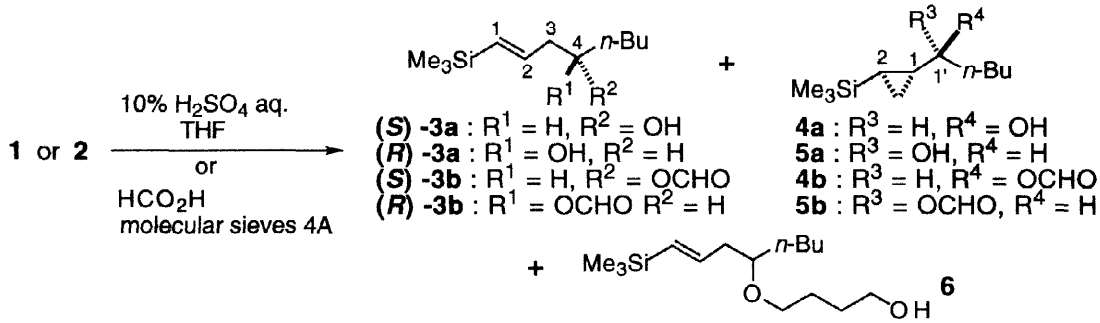


Table. Rearrangement of **1** and **2** under acidic conditions.

	Substrate	R^1	R^2	Condition[a]	Temp(°C)	Time(h)	(*S*)-**3**	: (*R*)-**3**	: **4**	: **5**	: **6** (%)
1	**1**	H	OH	A	rt	4	39	-	15	15	7
2	**1**	H	OH	B	rt	4	46	-	20	22	1
3	**2**	OH	H	A	rt	7	-	47	8	21	5
4	**2**	OH	H	B	rt	7	-	57	9	20	2
5	**1**	H	OCHO	C	8	4	20	-	25	35	-
6	**2**	OCHO	H	C	8	4	-	19	28	33	-

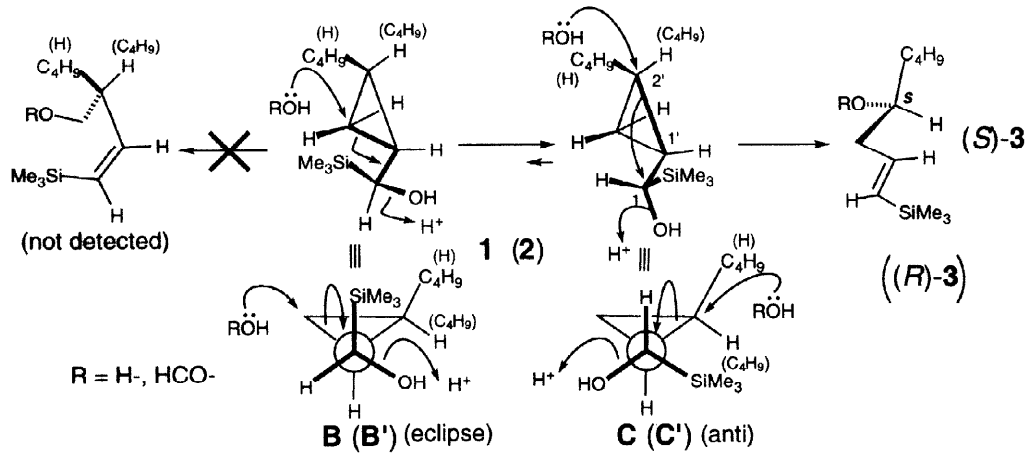
a) A: 10% H_2SO_4 (2 equiv), THF; B: 10% H_2SO_4 (20 equiv), THF; C: HCO_2H, molecular sieves 4A.

We next examined the solvolysis of the 2'*S* isomer **2** (87% ee) [1], which, upon treatment with the same conditions as that of **1**, produced a mixture of the silylcyclopropane **4a** and **5a** together with the *R* enantiomer of the vinylsilane **3a**. Treatment of **1** and **2** under the formolysis (HCO_2H, moleculer sieves 4A, or HCO_2H, Ac_2O) resulted in the formation of the corresponding formates **3b** - **5b**, respectively. [13] The yields of the silylcyclopropane **4b** and **5b** were slightly increased and those of the vinylsilane **3b** were decreased as compared with H_2SO_4. [14]

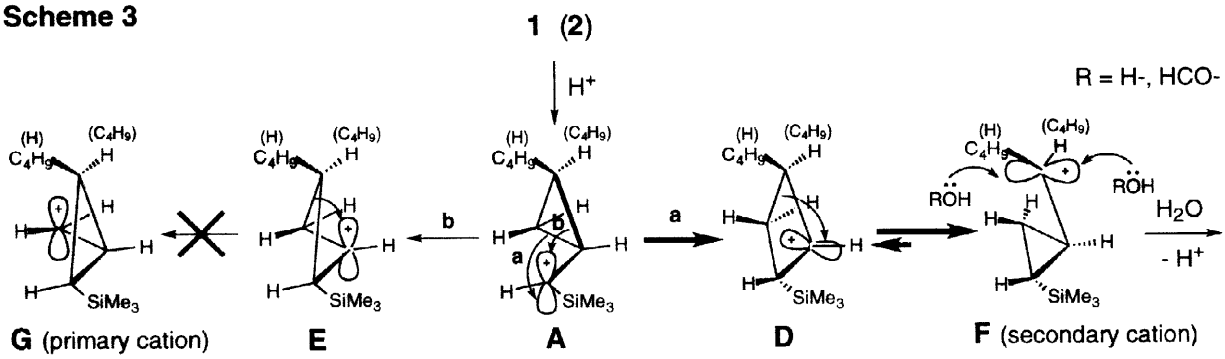
These experimental results led us to propose the following reaction pathways: (1) the formation of the vinylsilane **3** would be a stereospecific process (S_N2') via the conformer **C** (anti-periplanar conformation: the leaving hydroxyl group, the breaking bond, and the attacking hydroxyl group lie on an anti-periplanar relationship) which is thermodynamically much more favored than the conformer **B** (eclipse conformation: the TMS group is located at eclipse with the cyclopropane ring) (Scheme 2), [15] thus, the *S* isomer was produced from **1** and the *R* isomer from **2**, and (2) the formation of the mixture of diastereomeric **4** and **5** would be attributed to the tandem [1,2]-CC bond migration from the unstable α-trimethylsilyl cation **A** via a formation of the

putative cyclobutyl cation **D**, which immediately rearranged to the stable cyclopropylcarbinyl cation **F** (Scheme 3). Since none of the rearranged products derived from the primary cation **G** (path **b**) was obtained, the path **a** to form **D** would be the much more favored rearrangement process. Thus, the nucleophile (i.e., H_2O or HCO_2H) would attack the cationic center in a non-stereoselective manner to give the mixture of **4** and **5**.

Scheme 2

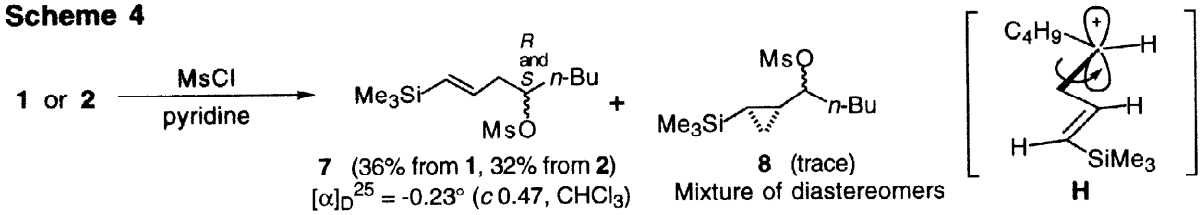


Scheme 3



Therefore, we assumed that the reaction proceeded in a competitive manner between the hydroxyl attack to the C2' position of **C** and the CC bond migration from **A**. The degree of its ratio is slightly affected by the reaction conditions. Since the α-hydroxycyclopropylsilanes would be reactive under the solvolytic conditions because of the electronic geminal interaction of the α-silyl effect, [16] the first step to form **A** would be significantly accelerated. The carbocationic rearrangement such as the ring expansion of a cyclopropylacylsilane to a cyclobutanone has been reported. [17] This is consistent with our proposed mechanism via the cyclobutyl cation. It is noted that the treatment of **1** or **2** with methanesulfonylchloride (MsCl) in pyridine at 0 °C afforded the mesylate **7**, which contained trace amounts of two diastereomers **8**. Surprisingly, the mesylate **7** was found to be racemic form (Scheme 4). [18] This result suggests the existence of the cation **H** which a methanesulfonyl anion attacked from both sides.

Scheme 4



In conclusion, it was found that the fate of the cationic species followed in a competitive

manner between the CC bond breaking of the cyclopropane ring (S_N2') and the migration of the cyclopropane ring via the putative cyclobutyl cation.

References and Notes

[1] Sakaguchi K, Mano H, Ohfune Y. Tetrahedron Lett. 1998;39:4311-4312.

[2] For reviews, see: [α- and β-silyl cations] (a) Bassindale AR, Taylor PG. In: Patai S, Rappoport Z, editors. The Chemistry of Organic Silicon Compounds Part 2. Chichester:John Wiley, 1989:Chapter14. [cyclopropylcarbinyl cation] (b) Richey Jr HG, Wiberg KB, Hess Jr AB, Ashe III AJ. In: Olah GA, Schleyer PvR, editors. Carbonium Ions. Vol. 3. Chichester:John Wiley, 1976:Chapter25,26.

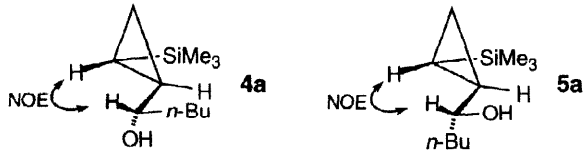
[3] For rearrangement of α-acyl-α-cyclopropyl-carbenium ion, see: Pardo C, Charpentier-Morize M. J. Chem. Soc., Chem. Commun. 1982;1037-1039.

[4] Small amounts of the vinylsilane **6**, which would be formed by a nucleophilic attack of 1,4-butanediol derived from THF, was by-produced. The absolute configuration of **6** was not determined. **6**: colorless oil, $[\alpha]_D^{20}$ -7.1° (*c* 1.0, $CHCl_3$) from **1**; $[\alpha]_D^{15}$ +6.0° (*c* 1.0, $CHCl_3$) from **2**.

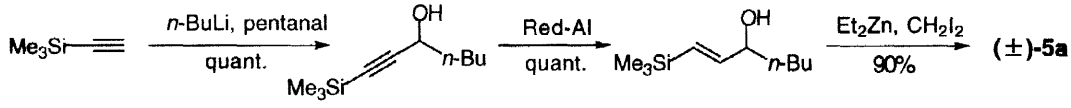
[5] The $AgNO_3$ pre-coated TLC plate was prepared by soaking commercially available TLC plate (Merck No. 1.05744.) in 20% $AgNO_3$ in CH_3CN and drying.

[6] Julia M, Julia S, Guegan R. Bull. Soc. Chim. France 1960;1072.

[7] The relationship between the substituents of cyclopropane was assigned to be *trans* by the observation of NOEs between the corresponding methine protones as shown below.

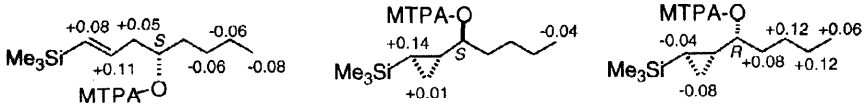


[8] The relative structures of **4a** and **5a** were confirmed by comparison with *rac*-**5** prepared as shown below.



[9] Yamaguchi S. In: Morrison JD, editor. Asymmetric Synthesis. Vol. 1. London:Academic Press, 1983:Chapter7.

[10] The $\Delta\delta$ value ($\delta_{(S)\text{-MTPA ester}} - \delta_{(R)\text{-MTPA ester}}$) of each MTPA ester is shown below. Ohtani I, Kusumi T, Kashman Y, Kakisawa H. J. Am. Chem. Soc. 1991;113:4092-4093.



[11] Physical constants and ^1H NMR data of (*S*)-**3a**, **4a**, and **5a**. (*S*)-**3a**: colorless oil, $[\alpha]_D^{19}$ +3.3° (*c* 2.0, $CHCl_3$, 99% ee); ^1H NMR (300 MHz, $CDCl_3$) δ6.00 (ddd, *J* = 6.6, 6.6, 18.5 Hz, 1 H), 5.76 (d, *J* =18.7 Hz, 1 H), 3.65 (m, 1 H), 2.35 (ddd, *J* = 5.6, 13.9 Hz, 1 H), 2.19 (ddd, *J* = 7.2, 7.2, 13.9 Hz, 1 H), 1.98 (br, 1 H), 1.20 - 1.70 (6 H), 0.90 (t, *J* = 7.0 Hz, 3 H), 0.05 (s, 9 H). **4a**: colorless oil, $[\alpha]_D^{24}$ -12.9° (*c* 0.31, $CHCl_3$, 99% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 2.88 (ddd, *J* = 6.3, 6.3, 7.8 Hz, 1 H), 1.53 - 1.60 (2 H), 1.20 - 1.45 (5 H), 0.88 (t, *J* = 7.3 Hz, 3 H), 0.76 (dddd, *J* = 4.7, 6.4, 6.4, 17.1 Hz, 1 H), 0.40 - 0.48 (2 H), -0.07 (s, 9 H), -0.48 (ddd, *J* = 6.8, 6.8, 10.0 Hz, 1 H). **5a**: colorless oil, $[\alpha]_D^{20}$ -18.5° (*c* 1.0, $CHCl_3$, 99% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 2.80 (ddd, *J* = 6.1, 6.1, 8.5 Hz, 1 H), 1.50 - 1.58 (2 H), 1.67 (br, 1 H), 1.18 - 1.44 (4 H), 0.88 (t, *J* = 7.1 Hz, 3 H), 0.76 (m, 1 H), 0.47 (ddd, *J* = 4.5, 4.5, 10.2 Hz, 1 H), 0.42 (ddd, *J* = 7.1, 7.1, 3.9 H z, 1 H), -0.08 (s, 9 H), -0.51 (ddd, *J* = 6.8, 6.8, 10.2 Hz, 1 H).

[12] The reaction using 20 equiv H_2SO_4 gave the same mixture where the total yields were increased (Table). The products **3a** - **5a** were found to be stable upon further treatment with the same reaction conditions. [19] This result indicates that the interconversion of the products did not occur.

[13] The formates **3b** - **5b** were identified by converting them into **3a** - **5a** by treatment with K_2CO_3 in MeOH, respectively.

[14] Treatment of **1** with $BF_3{\cdot}OEt_2$ and moleculer sieves 4A in $CDCl_3$ at -78 °C gave several less polar volatile olefinic products whose structures were not identified. The same result was obtained when **2** was employed.

[15] Brady SF, Ilton MA, Johnson WS. J. Am. Chem. Soc. 1968;90:2882-2889.

[16] Apeloig Y, Biton R, bu-Freih A. J. Am. Chem. Soc. 1993;115:2522-2523.

[17] (a) Danheiser RL, Fink D. Tetrahedron Lett. 1985;26:2513-2516. (b) Nakajima T, Segi M, Mitsuoka T, Fukute Y, Honda M, Naitou K. Tetrahedron Lett. 1995;36:1667-1670.

[18] Optically pure mesylate **7** was prepared from (*R*)-**3a** (99% ee) with MsCl in pyridine; $[\alpha]_D^{25}$ -11.9° (*c* 1.0, $CHCl_3$). This result suggests that none of the S_N2-type substitution occurred at C4 of the resulting mesylate **7** under the reaction condition.

[19] Several (TMS)cyclopropanes undergo facile ring-opening upon treatment with anhydrous HCl or $TiCl_4$ in dry CH_2Cl_2 at -78 °C. Daniels RG, Paquette LA. J. Org. Chem. 1981;46:2901-2910.