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Syntheses of Optically Active 2-Substituted Cyclopropanecarboxylic Acids from Chiral α-Hydroxysilane Derivatives

Kazuhiko Sakaguchi,* Hiroyuki Mano, and Yasufumi Ohfune*

Graduate School of Science, Department of Material Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

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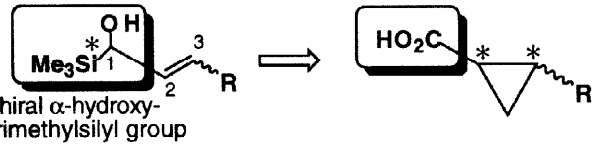
Abstract

Optically active 2-alkylcyclopropanecarboxylic acids were efficiently synthesized from the chiral α-hydroxytrimethylsilanes via a diastereoselective cyclopropanation as the key step.

Keywords: masked chirality; α-hydroxysilane; optically active cyclopropanecarboxylic acid; diastereoselective cyclopropanation

An optically active α-hydroxysilane group can be viewed as a masked chirality equivalent to an aldehyde or a carboxylic acid. [1] If this moiety connects with an allylic moiety at its C1 position, further diastereoselective carbon-carbon bond forming reactions to the allylic CC-double bond would be possible under participation of the neighboring hydroxy group. Very limited examples have been reported for the use of this type of α-hydroxysilanes such as the Ireland-Claisen rearrangement [2] and allylic transposition [3] despite the fact that versatile utility is expected of this moiety as a useful chiral synthon. In this report, we describe the syntheses of optically active cyclopropanecarboxylic acids, **6**, **9** and **13**, where the chirality of the α-hydroxysilanes **3** and **11** were completely transported to the newly formed stereogenic centers, respectively.



chiral α-hydroxy-trimethylsilyl group

The synthesis was begun with the preparation of the α-hydroxycyclopropylsilane **4**. Enantioselective reduction of the acylsilane **1** [4] with (-)-*B*-chloro diisopinocamphenylborane ((-)-DIP-Cl) [5] gave (*R*)-α-hydroxysilane **2** in 95% yield (99% ee), [6] which, upon reduction with the Lindlar catalyst, afforded the desired (1*R*,2*Z*)-allyl alcohol **3** (81%, *Z*/*E* = 18/1). The key cyclopropanation was performed using **3** with Et_2Zn-CH_2I_2. [7] The reaction proceeded in a highly stereoselective manner to give (1*R*,1'*R*,2'*S*)-**4** [8] as an exclusive diastereomer (97%). Swern oxidation of **4**, and subsequent oxidation of the resulting α-ketocyclopropylsilane **5** with H_2O_2-NaOH gave (1*R*,2*S*)-*cis*-2-butylcyclopropanecarboxylic acid **6** [8] (84% from **4**). The *trans* isomer **9** was prepared from the ester of **6** by inversion of its 1*R* ester group with $KN(TMS)_2$. [9] Hydrolysis of **8** gave the acid **9** [8]. Thus, both *cis*-**6** and *trans*-**9** were

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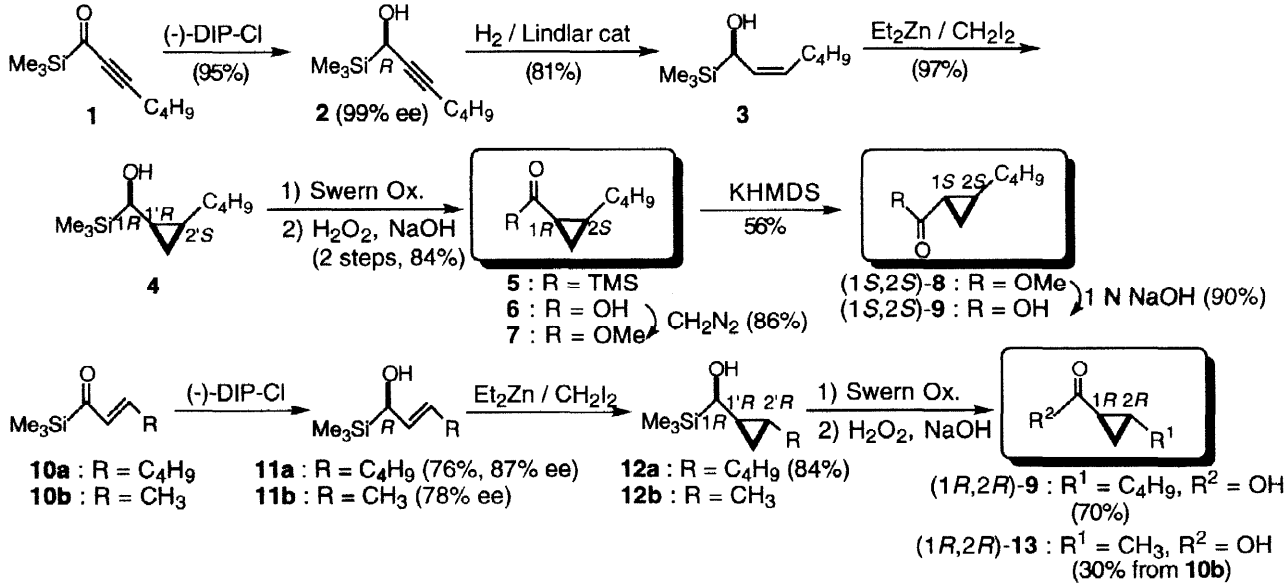
synthesized from **3**. The enantiomer of **9** was also synthesized from the (1*R*,2*E*)-allyl alcohol **11a** (87% ee), [6] prepared by an enantioselective reduction of the (*E*)-α-ketoallylsilane **10a** [10] with (-)-DIP-Cl (76%), in the same manner as the synthesis of **6** via the α-hydroxycyclopropylsilane (1*R*,1'*R*,2'*R*)-**12a** [8]. The use of 2-methyl derivative **11b** (78% ee) [6] yielded the (1*R*,2*R*)-*trans*-2-methylcyclopropanecarboxylic acid **13** [11].

Thus, optically active 2-alkylcyclopropanecarboxylic acids were efficiently synthesized from the chiral α-hydroxytrimethylsilane derivatives.



References and Notes

[1] Zweifel G, Backlund SJ. J. Am. Chem. Soc. 1977;99:3184-3185.

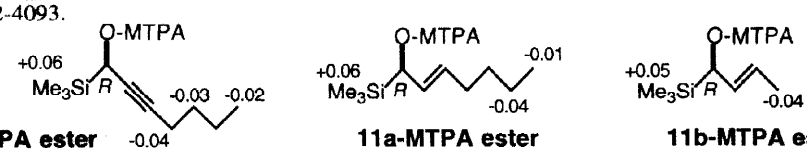
[2] Ireland RE, Varney MD. J. Am. Chem. Soc. 1984;106:3668-3670.

[3] Panek JS, Sparks MA. J. Org. Chem. 1990;55:5564-5566.

[4] Linderman RJ, Suhr Y. J. Org. Chem. 1988;53:1569-1572.

[5] (a) Soderquist JA, Anderson CL, Miranda EI, Rivera I. Tetrahedron Lett. 1990;31:4677-4680. (b) Dahr RK. Aldrichimica Acta 1994;27:43-51.

[6] The optical purity and absolute configuration of **2** and **11** were determined by the modified Mosher method, respectively. 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.



[7] (a) Charette AB, Lebel H. J. Org. Chem. 1995;60:2966-2967. (b) Landies YA, Rapado LP. Tetrahedron Lett. 1996;37:1205-1209.

[8] Physical constants and ^{1}H NMR data of **4**, **6**, **9**, and **12**. **4** (99% ee): colorless oil, $[\alpha]_D^{22}$ +41.5° (*c* 2.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (m, 1 H), 0.08 (s, 9 H), 0.71 (m, 1 H), 0.89 (t, *J* = 7.1 Hz, 3 H), 0.88 - 0.95 (2 H), 1.04 (m, 1 H), 1.25 - 1.45 (5 H), 1.55 (m, 1 H), 2.87 (d, *J* = 11.2 Hz, 1 H). **6** (99% ee): colorless oil, $[\alpha]_D^{21}$ -44.8° (*c* 1.78, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3 H), 0.96 (ddd, *J* = 4.9, 4.9, 7.3 Hz, 1 H), 1.07 (ddd, *J* = 4.3, 7.9, 7.9 Hz, 1 H), 1.25 - 1.40 (5 H), 1.50 - 1.60 (2 H), 1.67 (ddd, J = 5.5, 7.6, 8.8 Hz, 1H), 11.0 (br, 1 H). (1*S*,2*S*)-**9** (99% ee): colorless oil, $[\alpha]_D^{17}$ +82.2° (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, CDCl3) δ 0.76 (ddd, *J* = 4.0, 6.4, 8.1 Hz, 1 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 1.22 (ddd, *J* = 4.3, 4.3, 8.6 Hz, 1 H), 1.25 - 1.49 (8 H), 11.25 (br, 1 H). (1*R*,2*R*)-**9** (87% ee): $[\alpha]_D^{24}$ -76.3° (*c* 2.32, $CHCl_3$). **12** (87% ee): colorless oil, $[\alpha]_D^{24}$ +43.4° (*c* 2.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 0.29 (ddd, *J* = 4.6, 4.6, 7.6 Hz, 1 H), 0.37 (ddd, *J* = 4.4, 4.4, 8.8 Hz, 1 H), 0.59 (m, 1 H), 0.75 (dddd, *J* = 4.4, 4.4, 7.6, 10.7 Hz, 1 H), 0.88 (t, *J* = 7.0 Hz, 3 H), 1.04 (m, 1 H), 1.25 - 1.50 (5 H), 1.43 (m, 1 H), 2.46 (d, *J* = 10.8 Hz, 1 H).

[9] Shimamoto K, Ohfune Y. Synlett 1993;919-920.

[10] Compound **10** was prepared from the corresponding (2*E*)-allylic alcohols in the same manner as the reported method. Danheiser RL, Fink DM, Okano K, Tsai Y-M, Szczepanski SW. J. Org. Chem. 1985;50:5393-5396.

[11] **13** (78% ee): colorless oil, $[\alpha]_D^{14}$ -61.6° (*c* 1.64, EtOH). Bergman RG. J. Am. Chem. Soc. 1969;91:7405-7411.