Articles

A Stereochemical Study of the Isomerization of Cyclopropyl Ethers to Allyl Ethers Catalyzed with Zinc Iodide

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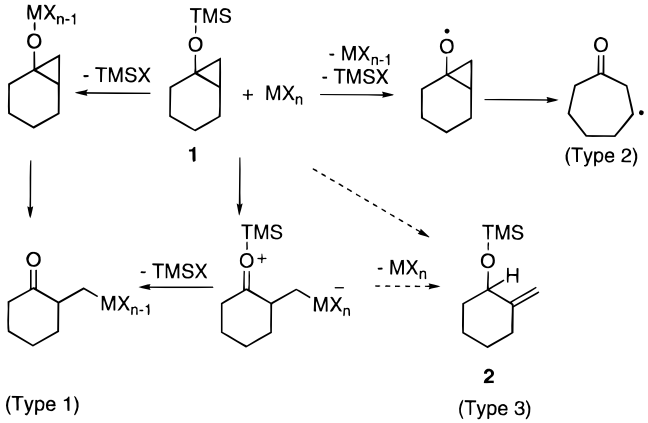
Optically active 1-alkoxybicyclo[4.1.0]heptane was converted using zinc iodide as a catalyst to 2-alkoxymethylidenecyclohexane without loss of optical purity. The mechanism of the isomerization was studied using a stereochemical analysis of the product and deuterium labeling experiments. The results indicated that the isomerization takes place through a stepwise mechanism that involves an attack of zinc iodide on the cyclopropane ring to cause ring opening, followed by an intramolecular 1,2-hydride shift with liberation of the zinc iodide.

Introduction

We have recently developed a novel and convenient method for the preparation of optically active cyclopropyl ethers by using 1,3-diols as a chiral linking bridge between a prochiral olefin and a zinc carbenoid.[1] The cyclopropyl ether function is a highly reactive site, because the strained C−C bond is activated by electron donation from the ether oxygen. The known reactions of a typical cyclopropyl ether **1** with inorganic salts as reagents or catalysts can be classified into three types.[2] The first group is the reaction through C1−C7 bond cleavage with desilylation giving the β-metallo ketone as a product or an intermediate (Scheme 1, type 1). The reactions with the salts of Cu(II),[3] Ag(I),[4] Hg(II),[5] Sn(IV),[6] Au(I),[7] Pd(II),[8] Pt(II),[9] etc. are in this category. The reactions in the second group are characterized by the oxidative cleavage of the Si−O bond using the salts of Fe(III)[10] followed by a C1−C6 bond cleavage to give the 3-cycloheptanoyl radical as an intermediate (type 2). The third group involving the isomerization *via* cleavage of the C1−C7 bond without the Si−O bond fission yielding

Scheme 1



2 is catalyzed by Zn(II),[11] Rh(I),[12] or Pt(II)[13] (type 3). The desilylation during the reactions of types 1 and 2 are easily understood by the nature of the weak Si−O bond, while the reaction of type 3 is highly unusual. For zinc iodide-promoted isomerization reactions, the synthetic scope has been thoroughly investigated, but the detailed mechanism of this type of reaction has not been clarified. The main questions include (1) the source of the hydrogen at the 1-position of **2** and whether it comes from a 1,2-hydrogen shift or an intermolecular reaction and (2) the role of zinc iodide and whether or not it adds to the C1−C7 bond giving an intermediate the same as in the reaction of type 1. Alkyl cyclopropyl ethers also undergo

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(1) (a) Sugimura, T.; Futagawa, T.; Tai, A. *Tetrahedron Lett.* **1988**, *29*, 5775. (b) Sugimura, T.; Futagawa, T.; Yoshikawa, M.; Tai, A. *Tetrahedron Lett.* **1989**, *30*, 3807. (c) Sugimura, T.; Yoshikawa, M.; Futagawa, T.; Tai, A. *Tetrahedron*, **1990**, *46*, 5955.

(2) For reviews, see: (a) Ryu, I.; Sonoda, N. *J. Syn. Org. Chem. Jpn.* **1985**, *43*, 112. (b) Nakamura, E. *J. Syn. Org. Chem. Jpn.* **1989**, *47*, 931. Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *133*, 1. (c) Kuwajima, I.; Nakamura, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed., Pergamon Press, Oxford, UK, 1991, Vol. 2, pp 441−454.

(3) Ryu, I.; Matsumoto, K.; Kameyama, Y.; Ando, M.; Kusumoto, N.; Ogawa, A.; Kambe, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1993**, *115*, 12330.

(4) (a) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192. (b) Ryu, I.; Suzuki, H.; Ogawa, A.; Kambe, N.; Sonoda, N; *Tetrahedron Lett.* **1988**, *29*, 6137.

(5) Ryu, I; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283.

(6) Nakahira, H.; Ryu, I.; Ikebe, M.; Oku, Y.; Ogawa, A.; Kambe, N.; Sonoda, N.; Murai, S. *J. Org. Chem.* **1992**, *57*, 17.

(7) Ito, Y.; Inouye, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41.

(8) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296.

(9) Ikura, K.; Ryu, I.; Ogawa, A; Sonoda, N.; Harada, S.; Kasai, N. *Organometallics* **1991**, *10*, 528.

(10) (a) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073. (b) Ito, Y.; Saegusa, T. *J. Org. Chem.* **1977**, *42*, 2326. (c) Ito, Y.; Fujii, S.; Nakatsuka, M.; Kawamoto, F.; Saegusa, T. *Organic Synthesis*, Norland, W. E., Ed.; Wiley: New York, **1988**; Collect. Vol. 6, p 327. (d) Booker-Milburn, K. I.; Thompson, D. F. *J. Chem. Soc. Perkin Trans. 1* **1995**, 2315.

(11) (a) Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1974**, *39*, 858. (b) Ryu, I.; Murai, S.; Sonoda, N. *Chem. Lett.* **1976**, 1049. (c) Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 1995. (d) Ryu, I.; Aya, T.; Otani, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279. (e) Schöllkopf, U.; Mittendorf, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 613.

(12) Ikura, K.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 6887.

(13) Ikura, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 1520.

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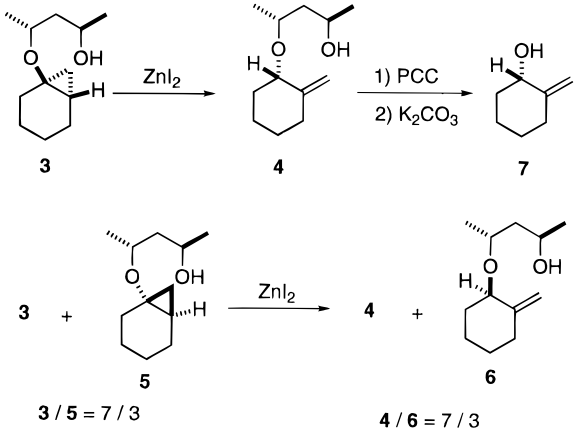
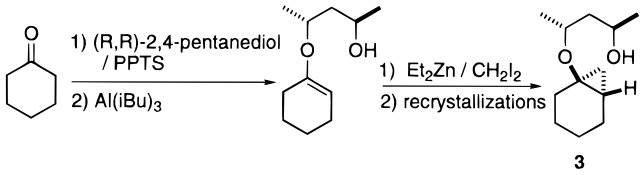
Scheme 2



the type 3 reaction under similar conditions.[11] In this study, by using an optically active alkyl cyclopropyl ether and its deuterated analogs, the stereochemistry of the reaction with zinc iodide was studied to clarify the isomerization mechanism.[14]

Results and Discussion

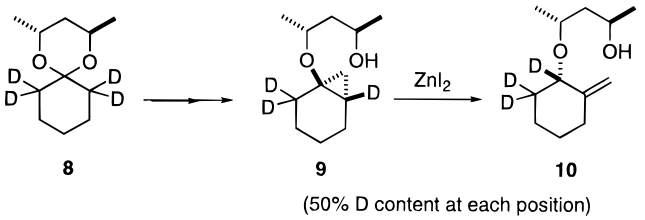
The optically active cyclopropyl ether **3** (>99% enantio- and diastereoisomeric purity) was prepared from cyclohexanone in three steps using our established method.[1]



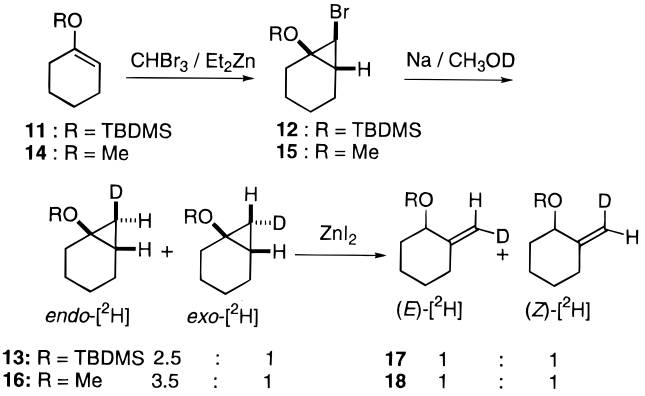
The reaction of **3** with freshly dried zinc iodide (3 equiv)[15] in dry benzene under reflux afforded **4** as a single diastereomer in 70% isolated yield. Under the same conditions, a mixture of diastereoisomers, **3** and **5** (**3**/**5** = 7/3), afforded a mixture of **4** and **6** in the same 7/3 ratio. Through these studies, it was determined that both diastereomers **3** and **5** stereospecifically afforded **4** and **6**, respectively. Thus, the chiral pentanediol moiety in the substrate did not participate in the stereocontrolled mechanism of the rearrangement and the stereochemistry of the cyclopropyl ether skeleton was fully conserved in the resulting allyl ether. The stereochemistry of **4** was assigned to be 2*S* by chemical correlation with (+)-(*S*)-**7**,[16] as shown in Scheme 2. The conservation of the stereochemistry with inversion at the ether chiral center strongly suggests the involvement of an intramolecular 1,2-hydride shift during the isomerization.[17]

To confirm the intramolecular 1,2-hydride shift mechanism, a deuterium labeling experiment was carried out with **9** (2,6-deuterated **3**, 50% deuterium content at each position) prepared from **8** by the reported method.[1] The

Scheme 3



Scheme 4



isomerization of **9** under the same reaction conditions as those used for **3** afforded **10**. The deuterium distribution in **10** was, as expected, at only the 1 and 6 positions. During the isomerization, the ratio of [6-^{2}H]-**9** and [6-^{1}H]-**9** monitored by ^{1}H-NMR did not changed. The regioselective deuterium shift with rigorous stereocontrol clearly showed that the isomerization of the cyclopropyl ether proceeded through an intramolecular 1,2-hydride shift (Scheme 3).

In order to clarify whether this 1,2-hydride shift occurs after the C1−C7 bond cleavage or if the shift and the cleavage occur synchronously, we next studied the stereochemical outcome through a rotation of the C6−C7 bond within the isomerization using the two deuterium labeling experiments as shown in Scheme 4.

A mixture of (*endo*)-[^{2}H]-**13** and (*exo*)-[^{2}H]-**13** in a ratio of 2.5/1 prepared from **11**[18,19] was subjected to isomerization with zinc iodide and diethylzinc in dichloromethane.[15] The reaction was accomplished in 2 days at room temperature without any detectable side reactions. The *E*/*Z* ratio of deuterium in **17** determined by ^{1}H-NMR was 1/1. Thus, the stereochemical purity at the 7-position of **13** was completely lost during the reaction. When **16** (*endo*-[^{2}H]/*exo*-[^{2}H] = 3.5/1) obtained from **14** was isomerized under the same conditions, the *E*/*Z* ratio of deuterium in **18** was again 1/1. The isomerization with no stereospecificity signifies a free rotation of the C6−C7 bond, which indicated the existence of an intermediate after the C1−C7 bond cleavage. Only a reasonable intermediate we could assume from natures of cyclopropyl ether and zinc iodide is a zwitterionic intermediate the same as that in type 1.

From the present study, it can be concluded that, in the presence of zinc iodide, cyclopropyl ether isomerizes to allyl ether through at least the following two steps: (1) cleavage of the C−C bond to form the adduct and (2) 1,2-hydride shift eliminating zinc iodide to produce a double bond (Scheme 5).

(14) A part of this work has been published as a communication: Sugimura, T.; Futagawa, T.; Ryu, I.; Tai, A. *J. Chem. Soc., Chem. Commun.* **1992**, 324.

(15) Zinc iodide is a highly hygroscopic reagent and absorbed water drastically decreases the reaction rate. The problem introduced by the use of commercially available zinc iodide was solved by using freshly dried commercial zinc iodide or by the addition of diethylzinc.

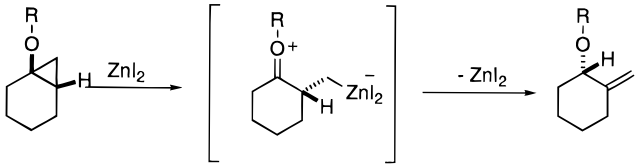
(16) Hoffmann, R. W.; Gerlach, R.; Goldmann, S. *Tetrahedron Lett.* **1978**, 2599.

(17) The inversion of the ether chiral center in the type 3 reaction was also reported during the isomerization with the Pt(II) salt. See ref 12.

(18) Miyano, S.; Matsumoto, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1975**, 364.

(19) Magarian, R. A.; Benjamin, E. J. *J. Pharm. Sci.* **1975**, *64*, 1626.

Scheme 5



The rate-determining step of the isomerization is probably the first C−C bond cleavage step, since no isotope effect was observed in the isomerization of **9** to **10**. This study is also significant from a synthetic point of view, since optically active allyl alcohol can be easily prepared from the prochiral ketone using the diastereodifferentiating cyclopropanation and the present stereospecific isomerization.

Experimental Section

General. ^{1}H-NMR (and ^{13}C-NMR) spectra were recorded at 400 MHz (and 100 MHz) using $CDCl_3$ as both a solvent and internal standard (7.26 and 77.1 ppm for $CHCl_3$). GLC analysis was conducted using a TC-WAX capillary column (60 m, 0.25 mm i.d.). MPLC was carried out using a pump (10 mL/min) and a Lobar column (MERCK Si-60 type B). All solvents were purified by distillation. All reactions were carried out in a dry N_2 atmosphere.

(2*S*,2′*R*,4′*R*)-2-Methylenecyclohexyl 2-(4-Hydroxypentyl) Ether (4). A solution of **3** (100 mg, >99% de) and anhydrous zinc iodide (450 mg) in dioxane (5 mL, distilled from benzophenone ketyl) was refluxed for 3 days. The mixture was extracted with ether, washed (2×) with aqueous ammonium chloride and ammonia, and dried (Na_2SO_4). The residue from the solvent evaporation was purified by MPLC on silica gel (30% ethyl acetate in hexane) giving **4** (70 mg) as a colorless oil. $[\alpha]_D^{20} = -16.2°$ (*c* 0.7, MeOH); ^{1}H-NMR δ 4.81 (bs, 2 H), 4.14 (m, 1 H), 3.88 (dd, J = 4.6, 3.2 Hz, 1 H), 3.79 (m, 1 H), 3.79 (m, 1 H), 2.88 (m, 1 H), 2.07 (ddd, J = 13.4, 4.9, 4.6 Hz, 1 H), 1.77−1.33 (m, 9H), 1.16 (d, J = 6.1 Hz, 3 H), 1.15 (d, J = 6.3 Hz, 3 H); ^{13}C-NMR δ 148.4, 109.6, 76.6, 69.8, 64.6, 44.8, 34.4, 32.0, 27.9, 23.5; MS *m*/*z* (M^+) calcd for $C_{12}H_{22}O_2$ 198.1601, obsd 198.1600.

(2*R*,2′*R*,4′*R*)-2-Methylenecyclohexyl 2-(4-Hydroxypentyl) Ether (6). A solution of a mixture of **3** and **5** (49.6 mg, **3**/**5** = 69/31, determined by capillary GLC) and anhydrous ZnI_2 (200 mg) in 5 mL of dry benzene was refluxed for 2 days. Analysis of the extract by capillary GLC indicated the ratio of **4** and **6** to be 68/28. The mixture was purified by MPLC on silica gel (elution with 30% ethyl acetate in hexane) giving **4** (23 mg) and **6** (12 mg). **6**: colorless oil, $[\alpha]_D^{20} = -34°$ (*c* 0.7, MeOH); ^{1}H-NMR δ 4.84 (s, 1 H), 4.77 (s, 1 H), 4.16 (m, 1 H), 3.88−3.84 (m, 2 H), 2.32 (m, 1 H), 2.04 (m, 1 H), 1.79−1.45 (m, 9 H), 1.20 (d, J = 6.1 Hz, 3 H), 1.18 (d, J = 6.1 Hz, 3 H); ^{13}C-NMR δ 149.4, 108.0, 78.2, 71.7, 64.7, 43.2, 34.3, 32.9, 28.0, 23.7, 22.7, 20.0; MS *m*/*z* (M^+) calcd for $C_{12}H_{22}O_2$ 198.1601, obsd 198.1597.

(*S*)-2-Methylenecyclohexanol (7). To a solution of **4** (20 mg) in 5 mL of dry CH_2Cl_2 was added PCC (55 mg) at rt. The mixture was stirred for 4 h, quenched with the addition of a small amount of H_2O, and filtered though a silica gel pad. The filtrate was concentrated and dissolved in MeOH (3 mL) with K_2CO_3 (20 mg). The mixture was stirred overnight and extracted with CH_2Cl_2. After reduction of the solvent to 1/10, the mixture was purified using preparative GLC (NPGS, 2 m, 90 °C) to give **7** (7 mg). $[\alpha]_D^{20} = 18°$ (*c* 0.1, ether) (lit.[16] $[\alpha]_D$ = 12.7° for 60% ee of (*S*)-**7**). The other spectroscopic data were identical with the reported data.

[2,2,6,6-^{2}H$_4$]Cyclohexanone (2*R*,4*R*)-2,4-Pentanediol Acetal (8). A solution of cyclohexanone (5 g) and K_2CO_3 (500 mg) in D_2O (10 mL, 99%) and anhydrous THF (3 mL) was stirred for 5 h at rt and then extracted with ether. The ^{1}H-NMR indicated that the incorporation of deuterium at the 2,6-positions was ca. 80%. A solution of deuterated cyclohexanone (2 g) and (*R*,*R*)-2,4-pentanediol (3 g) in benzene (80 mL) was refluxed overnight with a catalytic amount of PPTS using a Dean−Stark apparatus to collect the H_2O produced. The mixture was extracted and purified by silica gel column chromatography (75 g, 6% ethyl acetate in hexane) to give 1.49 g of **8**, which contained 50% of deuterium at the 2- and 6-positions (δ 1.64, m).

(2*S*,2′*R*,4′*R*)-1-([2,2′,6-^{2}H$_3$]Bicyclo[4.1.0]heptyl 2-(4-hydroxypentyl) ether (9). To a solution of **8** (640 mg) in anhydrous CH_2Cl_2 (36 mL) was added triisobutylaluminum (18.1 mL, 0.94 M in hexane) at 0 °C. After stirring for 1.5 h, the mixture was poured onto 1 N NaOH and extracted with CH_2Cl_2 (3×). The combined organic layer was washed with a 1 N NaOH (2×) and dried (Na_2SO_4). This concentration afforded 600 mg of **9**, which contained ca. 50% of deuterium at the 2- and 6-positions. The resulting enol ether (600 mg) was treated with diethylzinc (16.3 mL, 0.98 M in hexane) and diiodomethane (2.56 mL) in THF (20 mL). By using the reported purification method,[1c] 360 mg of **9** was obtained as colorless oil. The ^{1}H-NMR and ^{13}C-NMR of **9** indicated that it was free from the diastereomer and contained 50% deuterium at the 2- and 6-positions (δ 2.12, 1.98, and 1.23).

Isomerization 9 to 10 with Zinc Iodide. Using 95 mg of **9**, 55 mg of **10** was obtained by the method described for the preparation of **4**. The product isolated by MPLC was further purified by preparative GLC (NPGS, 2 m, 130 °C). The ^{1}H-NMR of **10** was identical to that of **4** except for the peak integration at δ 3.88 (0.5 H, H-1) and 1.77−1.33 (8 H, H-6,6′ was included). Under the same conditions, a mixture of **9** and **10** was also obtained by the shorter reaction of 24 h (50% conversion) or 48 h (90% conversion). In both cases, **9** in the mixture contained 50% deuterium at the 2- and 6-positions.

1-(*tert*-Butyldimethylsiloxy)-7-(*endo*)-bromobicyclo[4.1.0]heptane (12). To a solution of **11** (258.8 mg) in dry ether (5 mL) was added diethylzinc (6.1 mL, 1 M solution in hexane) at rt. After cooling to 0 °C, bromoform (1.1 mL) was added over 2 min. The mixture was warmed to rt and allowed to stand for 2 h. The reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with ether (20 mL, 6×). The mixture included two diastereomeric isomers, **12** and its *exo*-isomer (ratio = 2.5/1), the stereochemistries of which were determined by their coupling constants of H-7; $J_{6,7}$ = 4.6 Hz for **12** and $J_{6,7}$ = 9.5 Hz for the *exo*-isomer.

Purification by MPLC on silica gel (0.5% ethyl acetate in hexane) afforded 73.4 mg of **12** as a pale yellow oil. ^{1}H-NMR δ 2.62 (d, J = 4.6 Hz, 1 H), 2.13−1.97 (m, 2 H), 1.89 (m, 1 H), 1.62−1.43 (m, 2 H), 1.26−1.18 (m, 2 H), 1.05 (m, 1 H), 0.92 (s, 9 H), 0.18 (s, 3 H), 0.14 (s, 3 H); ^{13}C-NMR δ 57.2, 31.6, 31.4, 30.0, 25.9, 23.9, 21.6, 21.1, 18.2, −3.0, −3.6; MS *m*/*z* (M^+ − Br) calcd for $C_{13}H_{25}OSi$ 225.1675, obsd 225.1654.

[7-^{2}H]-1-(*tert*-Butyldimethylsiloxy)bicyclo[4.1.0]heptane (13). To a solution of **12** (178.1 mg) in dry ether (15 mL) was added sodium (1.17 g) followed by the addition of CH_3OD/D_2O (99% of ^{2}H, 30/1, 5 mL) at 0 °C. After extraction and MPLC purification on silica gel (1% ethyl acetate in hexane), a monodeuterated product **13** (81.2 mg, 66.1%) was obtained. The ^{1}H-NMR spectrum was identical with the reported nondeuterated compound except for the peak integration of H-7. The stereochemistries were determined by the coupling constants of H-7: $J_{6,7}$ = 6.3 Hz for (*endo*)-[^{2}H]-**13** and $J_{6,7}$ = 10.5 Hz for (*exo*)-[^{2}H]-**13**. ^{1}H-NMR δ 2.13−1.96 (m, 2 H), 1.88 (m, 1 H), 1.52−1.35 (m, 2 H), 1.32−1.19 (m, 2 H), 1.10−0.97 (m, 2 H), 0.85 (s, 9 H), 0.76 (d, J = 10.6 Hz, 0.29 H), 0.27 (d, J = 6.3 Hz, 0.71 H), 0.10 (s, 6 H); ^{13}C-NMR δ 56.2, 32.53 (and 32.51 for the diastereomer), 25.9, 24.71 (24.69), 22.0, 21.5, 19.5, 18.56 (J_{C-D} = 23.8 Hz, and 18.51, J_{C-D} = 23.8 Hz), 17.8, −3.2, −3.4; MS *m*/*z* (M^+) calcd for $C_{13}H_{25}DOSi$ 227.1816, obsd 227.1837.

1-Methoxy-7-(*endo*)-bromobicyclo[4.1.0]heptane (15). To a solution of 1-methoxycyclohexene (**14**, 700 mg) in dry hexane was added diethylzinc (1 M solution in hexane, 31 mL) followed by bromoform (5.45 mL) at 0 °C. The mixture was allowed to stand for 30 min and was extracted and purified by MPLC on silica gel (6% ethyl acetate in hexane), yielding 500 mg of **15** as a colorless oil. In this case, no endo product was detected. ^{1}H-NMR δ 3.42 (s, 3 H), 2.64 (dm J = 4.9 Hz, 1 H), 2.09−1.91 (m, 3 H), 1.63−1.39 (m, 3 H), 1.31−1.10 (m, 3 H); ^{13}C-NMR δ 61.7, 54.2, 30.6, 28.7, 26.3, 23.6, 21.4, 20.9; MS

m/*z* (M^+) calcd for $C_8H_{13}BrO$ 204.0150 and 206.0130, obsd 204.0155 and 206.0136.

[7-^{2}H]-1-Methoxybicyclo[4.1.0]heptane (16). To a solution of **16** (205 mg) in dry ether (25 mL) was added sodium (2 g) was added at 0 °C. A mixture of CH_3OD and D_2O (30/1, 8 mL) was added over a period of 1 h at the same temperature, extracted with pentane (2×), and washed with water. Most of the solvent was removed under a slightly reduced pressure, and the residue was purged on a preparative GLC (OV-101, 2 m, 90 °C). Its ^{1}H-NMR was identical to the authentic nondeuterated compound except for the peak integration at δ 0.83 and 0.24. The signals at the 7-position were assigned on the basis of the coupling constants and shift reagent experiment with Eu(fod)$_3$; the shift values ($\Delta\delta$) are cited in parentheses. ^{1}H-NMR δ 3.24 (s, 3 H, $\Delta\delta$ = 0.27), 2.07−1.90 (m, 3 H), 1.49 (m, 2 H), 1.26 (m, 1 H), 1.94−1.08 (m, 3 H), 0.83 (d, J = 10.7 Hz, 0.22 H, H-7 (*endo*), $\Delta\delta$ = 0.20), 0.24 (dd, J = 6.4, 5.1 Hz, 0.78 H, H-7(*exo*), $\Delta\delta$ = 0.14); ^{13}C-NMR δ 61.1, 53.4, 27.3, 24.6, 22.0, 21.4, 18.7, 17.0 (J_{C-D} = 24.2 Hz); MS *m*/*z* (M^+) calcd for $C_8H_{13}DO$ 127.1104, obsd 127.1089.

Isomerization of 13 and 16. Isomerization was carried out using the method discovered for the conversion of **1** to **2**. The product was isolated by MPLC on silica gel (hexane) for **17** (50−60% yield) and by preparative GLC (OV-101, 2 m, 90 °C) for **18** (ca. 70% yield). The spectra of **17** and **18** were fully identical with those of the nondeuterated compounds except for the integration of ^{1}H-NMR peaks. Since the olefin protons of **18** showed the same chemical shift at δ 4.82, Eu(fod)$_3$ was added to separate them into δ 4.87 and 4.85.

Supporting Information Available: ^{1}H-NMR spectra of **4**, **6**, **12**, **13**, **15**, and **16** and ^{13}C−NMR spectra of **12**, **13**, **14**, and **15** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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