12.57. Found: C, 60.00; H, 12,53.

1-Phenyl-1-(trimethylsilyl)methanol (4) (46%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 4.6 (s, 1 H), 7.3 (s, 5 H); IR (neat) (cm^{-1}) 3400 (br), 1590, 1250. Anal. Calcd for $C_{10}H_{16}OSi$: C, 66.61; H, 8.94. Found: C, 66.38; H, 8.99.

3-Phenyl-1-(trimethylsilyl)propan-1-ol (5) (40%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 1.90 (q, 2 H, J = 7 Hz), 2.85 (t, 2 H, J = 7 Hz), 3.40 (t, 1 H, J = 7.0 Hz), 7.25 (s, 5 H); IR (neat) (cm^{-1}) 3400 (br), 1590, 1250. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.02; H, 9.74.

1-Cyclohexyl-1-(trimethylsilyl)methanol (6) (19%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.8-1.9 (m, 11 H), 3.2 (d, 1 H, J = 7 Hz); IR (neat) (cm^{-1}) 3400 (br), 1450, 1250. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.44; H, 11.90. Found: C, 64.52; H, 11.89.

3-Phenyl-1-(trimethylsilyl)-2-propyn-1-ol (9) (76%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 4.3 (s, 1 H), 7.3 (br s, 5 H); IR (neat) (cm^{-1}) 3350 (br), 2200, 1590, 1480, 1250. Anal. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.75; H, 7.42.

1-(Trimethylsilyl)-2-heptyn-1-ol (10) (60%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.9 (br t, 3 H, J = 6 Hz), 1.2-1.7 (m, 4 H), 2.1-2.3 (m, 2 H), 4.05 (t, 1 H, J = 2 Hz); IR (neat) (cm^{-1}) 3400 (br), 1250. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 65.29; H, 10.96.

6-(Tetrahydropyranyloxy)-1-(trimethylsilyl)-2-heptyn-1-ol (11) (33%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 1.4-1.8 (m, 10 H), 2.1-2.3 (m, 2 H), 3.2-4.0 (m, 5 H), 4.55 (br s, 1 H); IR (neat) (cm^{-1}) 3400 (br), 1250; MS, m/z 284 (M^+).

1,3-Bis(trimethylsilyl)-2-propyn-1-ol (12) (73%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 18 H), 4.5 (s, 1 H); IR (neat) (cm^{-1}) 3350 (br), 1250; exact mass calcd for $C_9H_{20}OSi$ 200.1053, found 200.1054.

1-(Trimethylsilyl)-2-undecyn-1-ol (13) (75%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.8-1.0 (br t, 3 H, J = 6 Hz), 1.2-1.5 (m, 12 H), 2.1-2.3 (m, 2 H), 4.05 (m, 1 H); IR (neat) (cm^{-1}) 3400 (br), 1255. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.05; H, 11.76.

General Procedure for the Synthesis of Acylsilanes. The acylsilanes were obtained by oxidation of the (α-hydroxyalkyl)-silanes using the Swern oxidation procedure described earlier, omitting the nucleophilic addition step, and allowing the oxidation reaction mixture to warm to room temperature before aqueous quench. The known compounds **14**,[2a] **15**,[13b] and **16**[14] were obtained in 68%, 73%, and 55% yields, respectively.

3-Phenyl-1-(trimethylsilyl)-2-propyn-1-one (17) (69%): ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9 H), 7.2-7.5 (m, 5 H); IR (neat) (cm^{-1}) 2170, 1655, 1590, 1245; exact mass calcd for $C_{12}H_{14}OSi$ (M + H) 203.0891, found 203.0892.

1-(Trimethylsilyl)-2-heptyn-1-one (18) (71%): ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H), 0.9 (t, 3 H, J = 6 Hz), 1.3-1.6 (m, 4 H), 2.3-2.5 (m, 2 H); IR (neat) (cm^{-1}) 2150, 1580, 1240; exact mass calcd for $C_{10}H_{18}OSi$ 182.1127, found 182.1140.

6-(Tetrahydropyranyloxy)-1-(trimethylsilyl)-2-heptyn-1-one (19) (73%): ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9 H), 1.4-1.8 (m, 10 H), 2.3-2.5 (br t, 2 H, J = 6 Hz), 3.3-3.95 (m, 4 H), 4.4-4.5 (m, 1 H); IR (neat) (cm^{-1}) 2185, 1590, 1250; exact mass calcd for $C_{15}H_{26}O_3Si$ (M + H) 283.1736, found 283.1729.

1,3-Bis(trimethylsilyl)-2-propyn-1-one (20) (60%): ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 18 H); IR (neat) (cm^{-1}) 1590, 1250.

1-(Trimethylsilyl)-2-undecyn-1-one (21) (55%): ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9 H), 0.9 (t, 3 H, J = 6 Hz), 1.2-1.6 (m, 12 H), 2.2-2.4 (m, 12 H), 2.2-2.4 (m, 2 H); IR (neat) (cm^{-1}) 2190, 1590, 1250.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the research. We would also like to thank Dr. R. van Breemen for the exact mass determinations.

Registry No. 1, 106881-61-2; **3**, 112947-61-2; **4**, 17876-95-8; **5**, 112947-62-3; **6**, 66235-32-3; **7**, 95061-68-0; **8**, 95606-82-9; **9**, 112947-63-4; **10**, 112947-64-5; **11**, 112947-65-6; **12**, 112947-66-7; **13**, 112947-67-8; **14**, 5908-41-8; **15**, 61157-31-1; **16**, 112947-68-9; **17**, 112947-69-0; **18**, 112947-70-3; **19**, 112947-71-4; **20**, 86934-46-5; **21**, 112947-72-5; ClCOCOCl, 79-37-8; Me_3SiCH_2OH, 3219-63-4; *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-03-8; PhMgBr, 100-58-3; $PhCH_2CH_2MgBr$, 3277-89-2; c-$C_6H_{11}MgCl$, 931-51-1; CH_2CH-MgBr, 1826-67-1; *trans*-PhCHCHMgBr, 35672-47-0; PhC≡CLi, 4440-01-1; *n*-BuC≡CLi, 17689-03-1; $THPO(CH_2)_4C{\equiv}CLi$, 112947-73-6; $Me_3SiC{\equiv}CLi$, 54655-07-1; $C_8H_{17}C{\equiv}CLi$, 21433-46-5.

(14) Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495-5501.

Cyclizations of 2-(Allyldimethylsilyl)ethyl Radicals

Kazuhide Saigo,* Kazuo Tateishi, Hiroshi Adachi, and Yasushi Saotome

Central Research Laboratories, NEC Corporation, Miyamae-ku, Kawasaki 213, Japan

Received September 10, 1987

The cyclizations of 5-hexenyl radicals have attracted considerable interest, since the radicals strongly favor exo cyclization over endo cyclization, forming a thermodynamically unfavorable five-membered ring (Baldwin-Bechwith rules)[1] (Scheme I). It was explained in terms of the instability of the transition complex of endo mode. The introduction of a N atom[4] or an O atom[5] to 5-hexenyl radicals at the C-3 position enhances the rate of the exo mode, resulting in a greater preference for the five-membered ring. The cyclizations of 5-hexenyl radical analogues containing silicon have been studied. (Alloxydimethylsilyl)methyl radicals favor kinetically controlled exo cyclization,[6] while the direction of ring closure of 5-pentenylsilyl radicals is dependent on the substituents to a Si atom.[7] The cyclization of (3-butenyldimethylsilyl)methyl radical slightly favor endo mode.[8] We wish to report here the cyclizations of 5-hexenyl radical anologues substituted at the C-3 position by dimethylsilylene such as 2-(allyldimethylsilyl)ethyl radical (**1**) and 2-(allyldimethylsilyl)-propyl radical (**2**) (Scheme II).

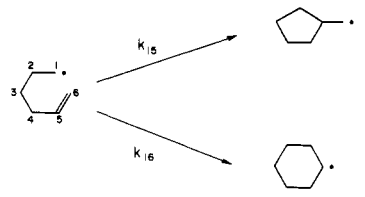
The two halides **6** and **8** were prepared as precursors[9] of the radicals. The straightforward preparations of **6** and **8** via **3**, **4**, **5**, and **7** are described in the Experimental Section.

Cyclizations were conducted under variety conditions[13] using Bu_3SnH and azobis(isobutyronitrile) (AIBN) as an initiator, although only one set of conditions will be reported here. No characteristic effect of condition change (e.g., solvent and reaction temperature) was observed. A solution of **6** (1 mmol), Bu_3SnH (1.2 mmol), and AIBN

(1) See reviews: Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.
(2) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, *15*, 2251.
(3) Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059.
(4) Kinny, R. J., Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.
(5) Beckwith, A. L. J.; Hawthorne, D. G.; Solomon, D. H. *Aust. J. Chem.* **1976**, *29*, 995.
(6) Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298.
(7) (a) See: Kochi, J. *Free Radicals*; Wiley: New York, 1973; Vol. 2, Chapter 27, p 793. (b) Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* **1984**, *106*, 3802.
(8) Wilt, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5251.
(9) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047.
(10) Michael, L.; Honek, J. F. *Tetrahedron Lett.* **1982**, *23*, 3249.
(11) (a) Weiss, R. G. *J. Org. Chem.* **1971**, *36*, 403. (b) Aneja, R.; Davies, A. P. Knaggs, J. A. *Tetrahedron Lett.* **1974**, *1*, 67.
(12) Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.
(13) The reaction temperature, the reaction time, and the mole ratio (halide compounds/Bu_3SnH) were changed in a range of 1-8 h, 60-80 °C, and 0.5-1.5, respectively. As solvents, benzene, and MEK were employed.

0022-3263/88/1953-1572$01.50/0

Scheme I

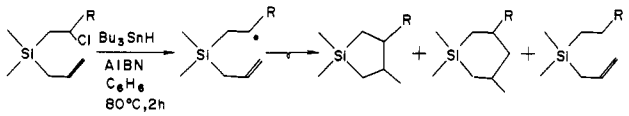


$k_{15}/k_{16} = k_{rel} > 200$[2] > 48[3]

Scheme II

1 2

Scheme III



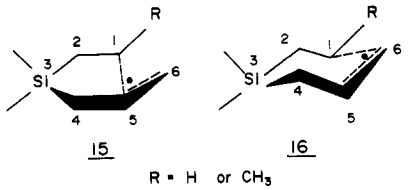
6, R=H 1 9 (0%) 10 (7%) 11 (83%)

8, R=CH_3 2 12 (0%) 13 (4%) 14 (61%)

(0.03 mmol) in 6 mL of benzene was sealed in an ampule and degassed by a freeze–pump–thaw method (four cycles). The ampule was dipped in an oil bath controlled at 80 °C for 2 h. The mixture was directly analyzed with GCMS on a 20% SE-30 on 60–80 mesh chromosorb W 3 mm i.d. × 2 m column at an oven temperature of 70 → 230 °C. The GC spectrum revealed that two major peaks were obtained. The two peaks were verified by the identity with those of 1,1-dimethylsilacyclohexane (**10**), which was commercially available, and of allyldimethylethylsilane (**11**), which was obtained by treatment of allylchlorodimethylsilane with ethylmagnesium bromide in ether (Scheme III). No peak attributed to 1,1,4-trimethylsilacyclopentane (**9**) was observed. The GC analysis indicates that the radical **1** cyclized through endo mode. The GC yield of **10**, calibrated from **10** and **11** prepared by authentic method, was 7% based on 90% reactive **6**.

The cyclization of **8** and the analysis of the products were conducted similarly. It was found that the GC spectrum also showed two peaks (retention time): (a) 3.04, (b) 3.60 min). The GC trace a was found to be the compound **14**, which was confirmed by the identity of the peak with that of authentic allyldimethyl-*n*-propylsilane (**14**) prepared by treatment of allylchlorodimethylsilane with propylmagnesium bromide in ether. The GC trace b was assigned to be the six-membered ring compound **13**, which was confirmed by the mass spectrum (*m/e* (relative intensity) 142 (M^+, 18), 127 (100), 99 (86), 95 (45), 72 (27), 51 (32), 43 (12)). In the case of six-membered ring compounds with a methyl groups such as methylcyclohexane, the prominent $(M - CH_3)^+$ peak is due to loss of the methyl substituent.[14] However, only half of the corresponding peak in methylcyclopentane arises in this manner, due to a greater degree of endocyclic cleavage in the five-membered ring.[14] Similar results were observed in the mass spectra of Si-containing five-membered ring and six-membered ring compounds.[15] When it comes to the mass spectrum of the GC trace b it is clear that the prominent peak $(M - CH_3)^+$ is *m/e* 127 due to loss of the methyl substituent, indicating that the compound shown in the GC trace b is assignable to six-membered ring compound **13**. The GC yield of **13** was 4% based on 65% reactive **8**.

Scheme IV



15 16

R = H or CH_3

The experimental results, in which the radicals **1** and **2** surprisingly favor endo cyclization over exo cyclization, may be associated with the length of Si–C bond (1.86 Å) and C–C bond (1.54 Å).[16] Because of the long Si–C bond, the distance of C-1–C-5 of complex **15** and C-1–C-6 of complex **16** are greater, compared with those for the 5-hexenyl radical (Scheme IV). When the two complexes **15** and **16** are compared, it seems that the complex **15** for exo mode is more strongly destabilized by strain than that for endo mode because of the long Si–C bond. Because, the complex **15** is consisted of a smaller ring such as five-membered ring. More tension should be required to constract the cyclic complex. Accordingly, the radicals **1** and **2** would undergo endo cyclization via the less strained transition complex to afford consequently six-membered ring compounds **10** and **13**.

Experimental Section

IR spectra were recorded with a Nippon Bunkoh A-3 spectrometer. ^1H NMR spectra, recorded in δ unit, were obtained with a Nippon Denshi A-60 spectrometer with TMS as internal reference. GCMS analyses were performed on a Shimadzu Auto GCMS 9020DF spectrometer with a 20% SE-30 on 60–80 mesh Chromosorb W 3 mm i.d. × 2 column at an oven temperature 70 → 230 °C. Elementary analyses were performed by Mistubishi-kasei Institute of Toxicological and Environmental Sciences.

Preparation of Allyl(chloromethyl)dimethylsilane (4). A 1-L three-necked flask with a mechanical stirrer was charged with magnesium turnings (13.4 g, 0.55 mol) and anhydrous ethyl ether (20 mL) under a dry nitrogen atmosphere. The magnesium was activated by addition of small amount (ca. 0.1 mL) of ethyl bromide. Anhydrous ethyl ether (400 mL) was added to the mixture, and then to a mixture was added allyl bromide (60.5 g, 0.5 mol) dropwise over a period of 2 h under a gentle reflux. Thereafter, the mixture was stirred at room temperature for further 2 h. The mixture was filtered off by using a glass-filter to remove unreacted magnesium. A solution of chloro(chloromethyl)dimethylsilane (**3**) (71.5 g, 0.5 mol) in anhydrous ethyl ether (100 mL) was placed in a 1-L, three-necked flask, and the solution was heated at gentle reflux. The ethereal allylmagnesium bromide solution prepared above was then added dropwise into the mixture over a period of 4 h under a gentle reflux, and the reaction was continued for an additional 1 h at reflux. After the mixture was chilled to room temperature, it was introduced into

(14) See: McLafferty, F. W. *Interpretation of Mass Spectra*, 2nd ed.; Benjamin: Reading, MA, 1973; p 103.

(15) Samples were either purchased from Petrarch Systems Inc. or obtained by authentic preparation method. 1, 1-Dimethylsilacyclopentane (*m/e* (relative intensity): 114(M^+, 37), 99 ($M-CH_3^+$, 81), 85 (100), 37 (35), 58 (56), 43 (17). 1, 1, 3-Trimethylsilacyclopentane (*m/e* (relative intensity): 128 (M^+, 13), 113 ($M - CH_3^+$, 13), 100 (100), 86 (59), 58 (63), 43 (26). 1, 1, 2, 5-Tetramethylsilacyclopentane (*m/e* (relative intensity): 142 (M^+, 25), 127 ($M - CH_3^+$, 13), 100 (100), 85 (100), 58 (20), 43 (15). 1, 1-Dimethylsilacyclohexane (*m/e* (relative intensity): 128 (M^+, 31), 113 ($M - CH_3^+$, 100), 85 (75), 72 (16), 59 (35).

(16) See: Robert, C. W. *Handbook of Chemistry and Physics*, 59th ed.; CRC: Boca Raton, FL, p F-215.

a dilute HCl aqueous solution. After extracting the mixture with ethyl ether, the ether fractions were combined and dried over anhydrous $MgSO_4$. The ether was evaporated, and then the residue was fractionally distilled to give **4** (30 g, 40%): bp 80 °C (83 mmHg); IR (neat) 1630, 1420, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 6 H), 1.8 (m, 2 H), 1.85 (s, 2 H), 4.8–6.3 (m, 3 H).

Anal. Calcd for $C_6H_{13}ClSi$: C, 48,50; H, 8.76. Found: C, 48.44; H, 8.89.

Preparation of Allyldimethyl(2-hydroxyethyl)silane (5). A 500-mL, three-necked flask was charged with magnesium turnings (4.16 g, 0.17 mol) and anhydrous ethyl ether (10 mL). The magnesium was activated by addition of ca 0.05 mL of ethyl bromide. To the mixture was added a solution of **4** (25.4 g, 0.17 mol) in anhydrous ethyl ether (100 mL) over a period of 4 h at gentle reflux. The reaction mixture was stirred for further 2 h at reflux. To the mixture was added paraformaldehyde (5.83 g) in small pieces over a period of 30 min and stirring continued for additional 1 h. The mixture was cooled and introduced into a dilute HCl aqueous solution. After extracting the mixture with ether the ether fractions were combined and dried over anhydrous $MgSO_4$. The ether was evaporated, and then the residue was fractionally distilled to give **5** (17.6 g, 72%): bp 110–104 °C (50 mmHg); IR (neat) 3330, 1630, 1040, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 6 H), 1.0 (t, 2 H), 1.75 (s, 1 H), 1.8 (m, 2 H), 3.85 (t, 2 H), 4.7–5.3 (m, 2 H), 5.5–6.3 (m, 1 H).

Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18. Found: C, 58.03; H, 11.11.

Preparation of Allyl(2-chloroethyl)dimethylsilane (6). A 300-mL, three-necked flask was charged with **5** (7.2 g, 0.05 mol), triphenylphosphine (17.05 g, 0.065 mol), and CCl_4 (45 mL) and the mixture stirred for 1 h at reflux. To the mixture was added hexane (50 mL) at room temperature. The precipitate appeared was filtered, and the filterate was concentrated in vacuo. The residue was fractionally distilled to provide **6** (6.2 g, 64%): bp 95–98 °C (105 mmHg); IR (neat) 1630, 1420, 500 cm^{-1}; ^1H NMR (CDCl[3) δ 0.15 (s, 6 H), 1.3 (m, 2 H), 1.6 (m, 2 H), 3.7 (m, 2 H), 4.7–5.3 (m, 2 H), 5.5–6.3 (m, 1 H).

Anal. Calcd for $C_7H_{15}ClSi$: C, 51.67; H, 9.29. Found: C, 51.80; H, 9.01.

Preparation of Allyldimethyl(2-hydroxypropyl)silane (7). A 300-Ml, three-necked flask was charged with magnesium turnings (2.9 g, 0.12 mol), anhydrous ethyl ether (10 mL), and ethyl bromide (0.1 mL), and then the mixture was allowed to warm to activate the magnesium. A solution of **4** (14.8 g 0.1 mol) in anhydrous ethyl ether (70 mL) was added dropwise over a period of 2 h at gentle reflux, and then the reaction was continued for an additional 2 h at room temperature. The mixture was chilled with an ice bath, and a solution of acetaldehyde (6.6 g, 0.15 mol) in ethyl ether (30 mL) was added dropwise over a period of 30 min. The mixture was thereafter stirred for an additional 30 min at room temperature and 4 h at reflux to complete the reaction. The mixture was allowed the cool to room temperature, and then the mixture was introduced into a dilute HCl aqueous solution and was extracted with ethyl ether (2 × 200 mL). The organic fractions were combined, washed with H_2O, dried (anhydrous $MgSO_4$), and evaporated. The residue was fractionally distilled to give **7** (13.1 g, 83%): bp 83–87 °C (20mmHg); IR (neat) 3350, 1630, 1420, 1020, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.1 (s, 6 H), 0.8 (d, 2 H), 1.3 (d, 3 H), 1.6 (m, 2 H), 1.8 (d, 1 H), 4.0 (m, 1 H), 4.6–5.1 (m, 2 H), 5.3–6.3 (m, 1 H).

Anal. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46. Found: 61.01; H, 11.42.

Preparation of Allyl(2-chloropropyl)dimethylsilane (8). A 100-mL, three-necked flask was charged with **7** (1.58 g, 0.01 mol) and CCl_4 (20 mL). To the mixture was added trioctylphosphine (3.70 g, 0.01 mol) over a period of 30 min at room temperature. After which time the mixture was concentrated in vacuo, and the residue was fractionally distilled to give **8** (0.4 g, 23%): bp 73 °C (18 mmHg); IR (neat) 1600, 1420, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 6 H), 1.3–1.5 (d, 2 H), 1.7 (d, 3 H), 1.85 (m, 2 H), 4.33 (m, 1 H), 4.6–5.2 (m, 2 H), 5.4–6.1 (m, 1 H).

Anal. Calcd for $C_8H_{17}ClSi$: C, 54.36; H, 9.69. Found: C, 54.47; H, 9.98.

Radical Cyclization of Allyl(2-chloroethyl)dimethylsilane (6). A 20-mL round-bottomed ampule was charged with **6** (0.162 g, 1.0 mmol), Bu_3SnH (0.35 g, 1.2 mmol), and benzene (6 mL), and the solution was degassed under vacuum by the freeze–pump–thaw method (four cycles). The ampule was immersed in an oil bath controlled at 80 °C. The reaction was continued for 4 h. The mixture was directly analyzed with GCMS.

Radical Cyclization of Allyl(2-chloropropyl)dimethylsilane (8). The radical cyclization of **8** was run in a similar manner to that of **6**. The compound **8** (0.176 g, 1.0 mmol), Bu_3SnH (0.35 g, 1.2 mmol) and benzene (6 mL) were employed. The GC trace showed the following compound (retention time, in min): benzene (1); a and b [small peaks] (2.5 and 3); (6); Bu_3SnH (16).

Registry No. **3**, 1719-57-9; **4**, 33558-75-7; **5**, 104107-86-0; **6**, 104107-85-9; **7**, 112988-53-1; **8**, 78847-25-3; **10**, 101772-53-6; **11**, 18292-34-7; **12**, 112988-54-2; **13**, 18293-92-0; 1,1-dimethylsilacyclopentane, 1072-54-4; 1,1,3-trimethylsilacyclopentane, 17936-93-5; 1,1,2,5-tetramethylsilacyclopentane, 55956-01-9; 1,1-dimethylsilacyclohexane, 4040-74-8.

Construction of an Enantiomerically Pure Cis-Fused 7-Oxabicyclo[4.3.0]nonan-3-one Skeleton. Synthesis of (1*S*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-one from D-Allose

Kin-ichi Tadano,* Masayuki Miyazaki, Seiichiro Ogawa,* and Tetsuo Suami†

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, Japan

Received July 28, 1987

In our previous papers, we reported several novel approaches directed toward the syntheses of enantiomerically pure highly oxygenated carbocycles starting from carbohydrates.[1] One of the newly developed approaches includes the transformation of D-glucose to (1*R*,6*R*,8*R*,9*R*)-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]non-4-en-3-one (**1**),[1c,f] which was readily converted to another chiral building block, 7-oxabicyclo[4.3.0]non-3-en-5-one derivative (**2**).[1h] The utility of compounds **1** and **2** was demonstrated by their stereoselective conversion to some enantiomerically pure pseudosugars.[1c,d,f,h] The construction of the trans-fused bicyclic compound **1** was achieved by an intramolecular aldol cyclization of a D-glucose-derived intermediate as the key reaction. In an extension of our interests in the intramolecular aldol cyclization of carbohydrate-derived intermediates, we report a synthesis of (1*S*,6*R*,8*R*,9*R*)-8,9-(isopropylidenedioxy)-7-oxabicyclo-[4.3.0]nonan-3-one (**3**) starting from the known 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**4**). Compound **3** possesses a cis stereochemistry at the ring juncture, which is not readily obtainable by our previous approaches.

Removal of the 5,6-*O*-isopropylidene group in compound **4**, which was prepared from D-glucose according to the reported procedure,[2] with 60% aqueous acetic acid gave compound **5**. The glycol cleavage[3] of compound **5** by periodate in aqueous methanol was followed by a Wittig olefination of the resulting 1,2-*O*-isopropylidene-α-D-*ribo*-pentodialdo-1,4-furanose (**6**) with (2-oxopropylidene)triphenylphosphorane[4] in refluxing benzene and resulted in the formation of three carbon extended (*E*)-α,β-unsaturated ketone **7** in 75% yield from **4**. Hy-

† Present address: Department of Chemistry, Faculty of Science and Technology, Meisei University, Hodokubo, Hino, Tokyo 191, Japan.

0022-3263/88/1953-1574$01.50/0