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

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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-

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drogenation of the enone **7** in the presence of Raney nickel T-4[5] gave a diastereomeric mixture of the saturated 7-hydroxy derivatives **8**. The ratio and the configuration at C-7 of the mixture were not determined. This mixture was converted to 5,6,8-trideoxy-1,2-*O*-isopropylidene-α-D-*erythro*-octo-1,4-furanos-3,7-diulose (**9**) by oxidation with pyridinium chlorochromate.[6] The intramolecular aldol cyclization of compound **9** to the 7-oxabicyclo[4.3.0]nonane derivative **10** was achieved in refluxing benzene in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]-undec-7-ene. After chromatographic purification of the reaction mixture on silica gel, compound **10** was obtained in 48% overall yield from compound **7**. The stereochemistry at C-1 of compound **10** was tentatively assigned to be *R* as depicted. This assignment was based on the sterically less hindered direction of demand for the attack of the anion generated at C-8 of compound **9** onto the carbonyl carbon (C-3). Treatment of compound **10** with excess methanesulfonyl chloride in pyridine at 50 °C gave the β-eliminated product **11** in 94% yield. Reduction of the carbonyl group in **11** with sodium borohydride proceeded from the β-face exclusively, and the (*R*)-hydroxyl derivative **12** was obtained in 86% yield. Hydrogenation of the olefin **12** in the presence of Raney nickel T-4[5] provided the cis-fused (1*S*,3*R*,6*R*,8*R*,9*R*)-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-ol (**13**) and the trans-fused 1*R*,3*R*,6*R*,8*R*,9*R* epimer **14** in 83% and 12% yields, respectively. The stereoselectivity of the hydrogenation is approximately 7:1 with preferential attack from the α-side. To establish the stereochemistry of the newly introduced chiral center (C-3) in compound **12**, the trans-fused compound **14** was benzoylated to give the 3-*O*-benzoyl derivative **16** in 77% yield. In the 400-MHz ^{1}H NMR spectrum of the conformationally rigid trans-fused **16**, H-6 appeared at δ 3.73 as a doublet of triplets with $J_{1,6} = J_{5ax,6} = 10.4$ Hz and $J_{5eq,6} = 3.4$ Hz, and H-3 appeared at δ 5.05 as a triplet of triplets with $J_{2ax,3} = J_{3,4ax} = 10.7$ Hz and $J_{2eq,3} = J_{3,4eq} = 4.3$ Hz. These results supported the assignment of the configuration at C-3 in compound **16** and therefore of compounds **12**–**14** as a *R* as depicted. Pyridinium chlorochromate oxidation of the alcohol **13** gave the title compound **3** in 92% yield. On the other hand, pyridinium chlorochromate oxidation of the alcohol **14** gave quantitatively (1*R*,6*R*,8*R*,9*R*)-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-one (**15**), which was identical with an authentic sample[1c,f] in IR and ^{1}H NMR spectra. Therefore, we have achieved a practical synthesis of the enantiomerically pure cis-fused 7-oxabicyclo[4.3.0]nonane skeleton.[7]

Experimental Section

General Methods. Reactions were carried out at room temperature unless otherwise stated. The reaction mixtures and the combined extracts were concentrated in vacuo by an evaporator at 30–40 °C with a bath. Melting points were determined with a Mitamura Riken micro melting point apparatus and are uncorrected. Specific rotations were measured by a Jasco DIP-4 polarimeter in chloroform solution with a 10-mm cell. Column chromatography was performed with silica gel 60 (Katayama Chemicals, K070) and thin layer chromatography (TLC) on glass plates coated with Kieselgel 60 GF_{254} (Merck), followed by UV light detection and charring with sulfuric acid. IR spectra were recorded with a Hitachi 225 spectrometer. ^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) or JEOL JMN-GX400 FT NMR (400 MHz) spectrometers for $CDCl_3$ solutions with an internal standard of tetramethylsilane.

Benzene was dried over $CaCl_2$ and then distilled over $LiAlH_4$. Dichloromethane (CH_2Cl_2) was distilled over CaH_2. Pyridine was distilled over NaOH.

1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranose (4). This compound was prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in 82% yield according to the reported procedure:[2] mp 70–71 °C, lit.[2] mp 77–78 °C; $[\alpha]^{18}_D$ +27.0° (*c* 0.47, H_2O).

(*E*)-5,6,8-Trideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-oct-5-eno-1,4-furanos-7-ulose (7). A solution of compound **4** (25.0 g, 96.0 mmol) in 60% aqueous acetic acid (370 mL) was stirred for 12 h and then concentrated to give 1,2-*O*-isopropylidene-α-D-allofuranose (**5**) (TLC R_f 0.20, ethanol/toluene = 1:5). To a stirred solution of this crude material in methanol (300 mL) at 0 °C was added an aqueous solution (70 mL) of sodium periodate (22.6 g, 106 mmol). After 15 min, the mixture was concentrated. To the residue was added CH_2Cl_2 (100 mL), and the resulting solids were removed by filtration and then washed with CH_2Cl_2 (100 mL × 4). The combined filtrate and washings were concentrated to give 1,2-*O*-isopropylidene-α-D-*ribo*-pentodialdo-1,4-furanose (**6**) (21.9 g; TLC R_f 0.41, ethanol/toluene = 1:5). A solution of the crude aldehyde **6** and (2-oxopropylidene)triphenylphosphorane (52.0 g, 163 mmol) in benzene (300 mL) was refluxed for 1 h and then concentrated. The residue was partitioned between CH_2Cl_2 (300 mL) and water (300 mL). The aqueous layer was extracted with CH_2Cl_2 (300 mL × 2). The organic layers were dried over Na_2SO_4 and then concentrated. The residue was chromatographed on silica gel (300 g, ethyl acetate/hexane = 1:3) and the fraction corresponding to R_f 0.51 (ethanol/toluene = 1:5) was concentrated to give crystalline **7**, which was recrystallized from ethyl acetate/hexane = 1:2 to give 16.5 g (75%) of compound **7** as colorless needles, mp 105–107 °C: $[\alpha]^{19}_D$ +54.9° (*c* 1.14); IR ν^{KBr}_{max} 3460, 2990, 1675, 1630, 1400, 1380, 1250, 1210, 1165, 1120, 1095 cm^{-1}; ^{1}H NMR δ 1.36, 1.57 (3 H × 2, each s, $C(CH_3)_2$), 2.27 (3 H, s, $COCH_3$), 2.87 (1 H, d, J = 10 Hz, OH), 3.61–3.88 (1 H, m, H-3), 4.27–4.44 (1 H, m, H-4), 4.62 (1 H, t, J = 4.5 Hz, H-2), 5.85 (1 H, d, J = 4.5 Hz, H-1), 6.34 (1 H, dd, J = 2 and 16.5 Hz, H-6), 6.82 (1 H, dd, J = 4 and 16.5 Hz, H-5). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.02; H, 6.96.

(1*R*,6*R*,8*R*,9*R*)-1-Hydroxy-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-one (10). A solution of compound **7** (8.00 g, 35.0 mmol) in ethanol (100 mL) was hydrogenated in the presence of Raney nickel T-4 under atmospheric hydrogen pressure for 24 h. The catalyst was removed with a Celite pad and then the catalyst was washed with ethanol. The combined filtrate and washings were concentrated to give a diastereomeric mixture of **8** (8.60 g; TLC R_f 0.30, ethanol/toluene = 1:5), which was oxidized without separation. To a stirred solution of the

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(5) Nishimura, S. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 61.

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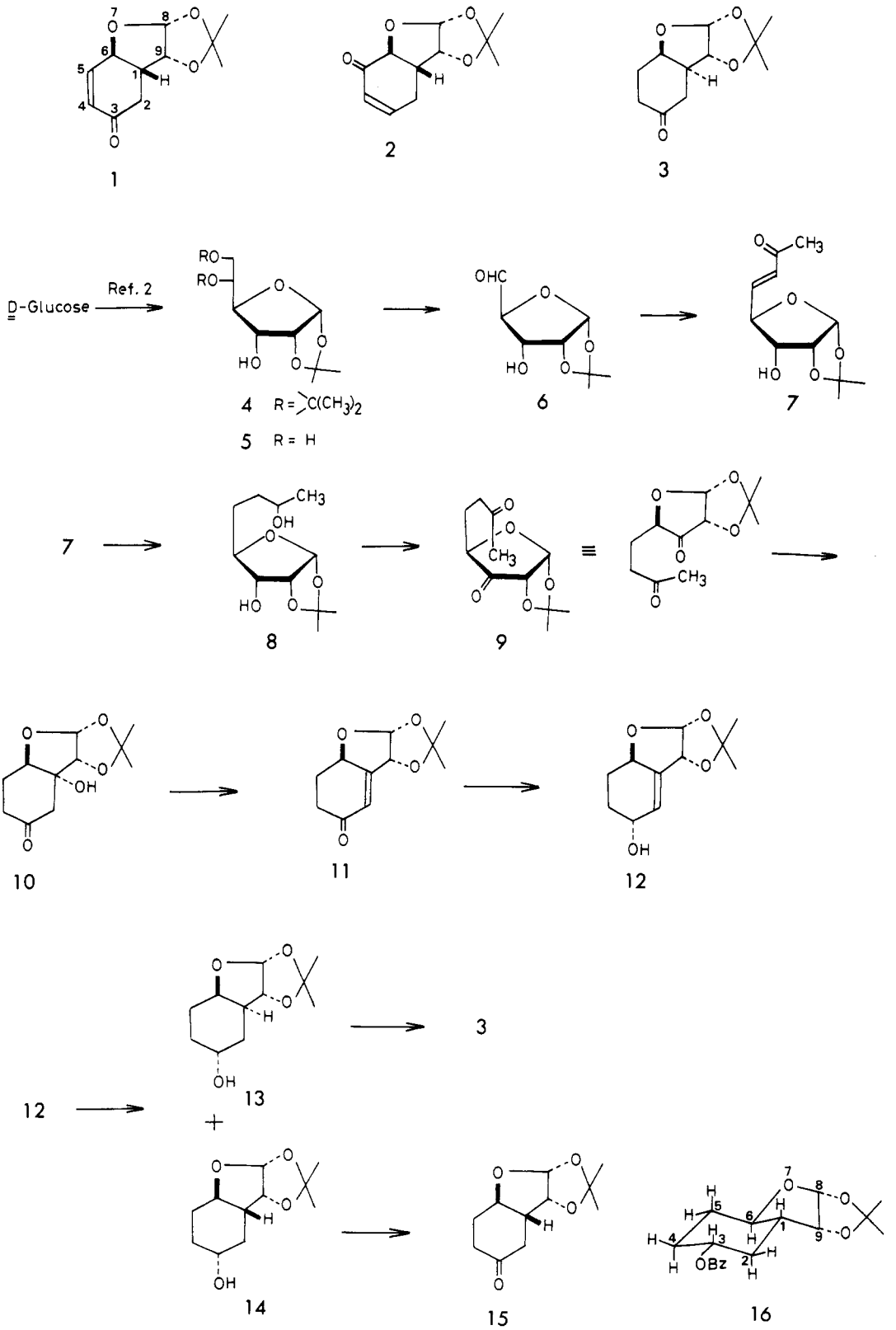
(7) Hydrogenation of compound **11** in the presence of Raney nickel T-4 gave a diastereomeric mixture of the saturated 3-hydroxyl derivatives, which was converted to compounds **3** and **15** by pyridinium chlorochromate oxidation. Unfortunately, the ratio of the ketones **3** and **15** was approximately 1:1. This result would indicate that the hydrogenation of the olefin of compound **11** was nonstereoselective. Additionally, hydrogenation of protected forms of compound **12** also gave unsatisfactory results. The *O*-benzoyl derivative of the alcohol **12** was converted to the cis-fused **13** and the trans-fused **14** in an approximately 4:1 ratio by hydrogenation and then O-debenzoylation. Hydrogenation of the *O*-(*tert*-butyldiphenylsilyl) derivative of the alcohol **12** also proceeded nonstereoselectively to give a 1:1 saturated mixture.

Scheme I



mixture **8** in CH_2Cl_2 (100 mL) were added pyridinium chlorochromate (30.2 g, 140 mmol) and molecular sieves (4A, powder, 30 g). After being stirred for 14 h, the mixture was concentrated. The residue was applied onto a silica gel column (200 g), and the column was then eluted with ether. The ethereal fraction corresponding to R_f 0.43 (ethanol/toluene = 1:5) was concentrated to give crystalline **9** (4.70 g): ^{1}H NMR δ 1.39, 1.50 (3 H × 2, each s, $C(CH_3)_2$), 1.65–2.25 (2 H, m, H-5,5′), 2.16 (3 H, s, $COCH_3$), 2.60 (2 H, t, J = 7.5 Hz, H-6,6′), 4.29–4.48 (2 H, m, H-2,4), 6.00 (1 H, d, J = 4.5 Hz, H-1). A solution of compound **9** (4.70 g) in benzene (70 mL) containing 1,8-diazabicyclo[5.4.0]undec-7-ene (0.31 mL, 2.06 mmol) was refluxed for 3 h and the mixture was then concentrated. The residue was partitioned between CH_2Cl_2 (70 mL) and water (70 mL), and the aqueous layer was extracted with CH_2Cl_2 (70 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was chromatographed by using silica gel (50 g, ethanol/toluene = 1:40), and the fraction corresponding to R_f 0.41 (ethanol/toluene = 1:8) was concentrated to give crystalline **10** (3.81 g, 48%), mp 132–133 °C: $[\alpha]^{20}_D$ +50.3° (c 0.88); IR ν^{KBr}_{max} 3460, 2990, 1700, 1380, 1375, 1305, 1265, 1250,

1205, 1170, 1065 cm^{-1}; ^{1}H NMR δ 1.37, 1.58 (3 H × 2, each s, C(CH$_3$)$_2$), 2.07–2.57 (6 H, m, H-H-2,2′,4,4′,5,5′), 2.80 (1 H, s, OH), 4.00 (1 H, t, J = 3 Hz, H-6), 4.14 (1 H, d, J = 4.5 Hz, H-9), 5.86 (1 H, d, J = 4.5 Hz, H-8). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.69; H, 7.06.

(6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]non-1-en-3-one (11). To a stirred solution of compound **10** (3.69 g, 16.2 mmol) in pyridine (37 mL) were added methanesulfonyl chloride (2.51 mL, 32.4 mmol) and 4-(dimethylamino)pyridine (396 mg, 3.24 mmol). The mixture was stirred for 4 h and then heated at 50 °C for 26 h. The mixture was coevaporated with toluene to remove pyridine completely. The residue was partitioned between CH_2Cl_2 (60 mL) and water (60 mL). The aqueous layer was extracted with CH_2Cl_2 (60 mL × 2). The combined organic layers were dried over Na_2SO_4 and then concentrated. The residue was chromatographed on silica gel (100 g, ethyl acetate/hexane = 1:7), and the fraction corresponding to R_f 0.44 (ethanol/toluene = 1:8) was concentrated to give crystals of compound **11** (3.20 g, 94%), mp 107–108 °C: $[\alpha]^{20}_D$ +148.6° (*c* 1.14); IR ν^{KBr}_{max} 2990, 2940, 2860, 1685, 1385, 1375, 1330, 1250, 1235, 1215, 1160, 1085, 1050, 1015 cm^{-1}; ^{1}H NMR δ 1.40, 1.57 (3 H × 2, each s, C(CH$_3$)$_2$), 1.67–2.67 (4 H, m, H-4,4′,5,5′), 4.89 (1 H, t, J = 6 Hz, H-6), 5.02 (1 H, d, J = 4.5 Hz, H-9), 5.96 (1 H, d, J = 4.5 Hz, H-8), 6.08 (1 H, s, H-2). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.75. Found: C, 62.97; H, 6.68.

(3*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]non-1-en-3-ol (12). To a stirred solution of compound **11** (3.20 g, 15.2 mmol) in ethanol (110 mL) at 0 °C was added sodium borohydride (403 mg, 10.6 mmol). After being stirred at the same temperature for 30 min, the reaction mixture was then neutralized with 1 M aqueous HCl solution. The mixture was concentrated and the residue partitioned between CH_2Cl_2 (70 mL) and water (70 mL). The aqueous layer was extracted with CH_2Cl_2 (70 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (140 g, ethyl acetate/hexane = 1:3), and the fraction corresponding to R_f 0.37 (ethanol/toluene = 1:8) was concentrated to give crystals of compound **12** (2.79 g, 86%), mp 108–109 °C: $[\alpha]^{21}_D$ +122.7° (*c* 1.18); IR ν^{KBr}_{max} 3260, 3000, 2940, 2880, 1370, 1250, 1200, 1165, 1150, 1050 cm^{-1}; ^{1}H NMR δ 1.32, 1.50 (3 H × 2, each s, C(CH$_3$)$_2$), 1.22–1.55 (2 H, m, H-4,4′ or H-5,5′), 1.95–2.35 (2 H, m, H-5,5′ or H-4,4′), 2.90–3.30 (1 H, br s, OH), 4.15–4.40 (1 H, m, H-3 or H-6), 4.40–4.70 (1 H, m, H-6 or H-3), 4.79 (1 H, d, J = 4.5 Hz, H-8), 5.74 (1 H, d, J = 4.5 Hz, H-9), 5.86 (1 H, br s, H-2). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.39; H, 7.50.

(1*S*,3*R*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-ol (13 and 14). A solution of compound **12** (2.79 g, 13.1 mmol) in ethanol (40 mL) was hydrogenated in the presence of Raney nickel T-4 under atmospheric hydrogen pressure for 18 h. The catalyst was removed with a Celite pad and then the catalyst was washed with ethanol. The combined filtrate and washings were concentrated. The residue was chromatographed on silica gel (110 g, ethyl acetate/hexane = 1:4). The fraction corresponding to R_f 0.27 (ethanol/hexane = 1:8) was concentrated to give crystals of compound **13** (2.34 g, 83%), mp 122–123 °C. The fraction corresponding to R_f 0.23 was concentrated to give crystals of compound **14** (0.341 g, 12%), mp 74–76 °C. **13**: $[\alpha]^{22}_D$ −3.7° (*c* 1.28); IR ν^{KBr}_{max} 3470, 2960, 2940, 1385, 1375, 1260, 1205, 1170, 1060 cm^{-1}; ^{1}H NMR δ 1.30, 1.49 (3 H × 2, each s, C(CH$_3$)$_2$), 1.50–2.50 (7 H, m, H-1,2,2′,4,4′,5,5′), 2.59 (1 H, br s, OH), 4.05 (1 H, t, J = 2.5 Hz, H-6), 4.20 (2 H, br d, J = 4 Hz, H-3,9), 5.78 (1 H, d, J = 4 Hz, H-8). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.89; H, 8.33. **14**: $[\alpha]^{23}_D$ +15.2° (*c* 0.80); IR ν^{KBr}_{max} 3420, 3000, 2950, 2880, 1460, 1380, 1270, 1250, 1210, 1170, 1130, 1110, 1090 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.33, 1.53 (3 H × 2, each s, C(CH$_3$)$_2$), 1.30–1.51, 2.05–2.17 (5 H, 3 H, each m, H-1,2,2′,4,4′,5,5′, OH), 3.66 (1H, dt, $J_{1,6}$ = $J_{5ax,6}$ = 10.7 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6), 3.71–3.79 (centered at δ 3.75, 1 H, m, H-3), 4.55 (1 H, t, $J_{1,9}$ = $J_{8,9}$ = 3.9 Hz, H-9), 5.84 (1 H, d, $J_{8,9}$ = 3.9 Hz, H-8). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.91; H, 8.35.

(1*S*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]nonan-3-one (3). To a stirred solution of the alcohol **13** (40.6 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) were added pyridinium chlorochromate (61 mg, 0.28 mmol) and molecular sieves (60 mg). After 1 h, the mixture was concentrated. The residue was chromatographed on silica gel (1 g) and the column was eluted with ether. The ethereal fraction corresponding to R_f 0.42 (ethanol/toluene = 1:8) was concentrated to give crystals of the ketone **3** (37.0 mg, 92%), mp 82–84 °C: $[\alpha]^{23}_D$ +7.3° (*c* 0.83); IR ν^{KBr}_{max} 2990, 2980, 2920, 1715, 1380, 1370, 1250, 1200, 1170, 1145, 1080 cm^{-1}; ^{1}H NMR δ 1.31, 1.52 (3 H × 2, each s, C(CH$_3$)$_2$), 1.85–2.77 (7 H, m, H-1,2,2′,4,4′,5,5′), 4.33–4.51 (2 H, m, H-6,9), 5.92 (1 H, d, J = 4.5 Hz, H-8). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.48; H, 7.66.

(1*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]nonan-3-one (15). Compound **14** (23.0 mg, 0.10 mmol) was oxidized with pyridinium chlorochromate (46 mg) in the presence of molecular sieves (50 mg) in CH_2Cl_2 (1 mL) for 10 h. After chromatographic purification on silica gel (1 g), crystals of the ketone **15** (22.7 mg, quantitative) were obtained from the ethereal fraction of R_f 0.67 (ethanol/toluene = 1:8), mp 96.5–98 °C (lit.[1c,f] mp 98–98.5 °C): $[\alpha]^{17}_D$ −28.8° (*c* 1.05), [lit.[1c,f] $[\alpha]^{21.5}_D$ −33.7° (*c* 1.66)]. The IR and ^{1}H NMR spectra of compound **15** were identical with those of an authentic sample.[1c,f]

(1*R*,3*R*,6*R*,8*R*,9*R*)-3-(Benzoyloxy)-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonane (16). To a stirred solution of compound **14** (14.5 mg, 0.07 mmol) in pyridine (0.5 mL) at 0 °C was added benzoyl chloride (0.012 mL, 0.1 mmol). After being stirred for 1.5 h at the same temperature, the mixture was concentrated. The residue was partitioned between CH_2Cl_2 (10 mL) and water (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were dried over Na_2SO_4 and then concentrated. The residue was chromatographed on silica gel (1.5 g, ethyl acetate/hexane = 1:15), and the fraction corresponding to R_f 0.32 (ethanol/toluene = 1:15) was concentrated to give crystals of compound **16** (16.5 mg, 77%), mp 95–96 °C: $[\alpha]^{24}_D$ +29.1° (*c* 0.83); IR ν^{KBr}_{max} 2990, 2980, 2960, 2900, 2870, 1720, 1450, 1385, 1370, 1335, 1320, 1270, 1260, 1245, 1220, 1180, 1165 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.32, 1.53 (3 H × 2, each s, C(CH$_3$)$_2$), 1.47–1.76, 2.21–2.34 (4 H, 3 H, each m, H-1,2,2′,4,4′,5,5′), 3.73 (1 H, dt, $J_{1,6}$ = $J_{5ax,6}$ = 10.4 Hz, $J_{5eq,6}$ = 3.4 Hz, H-6), 4.59 (1 H, t, $J_{1,9}$ = $J_{8,9}$ = 3.4 Hz, H-9), 5.05 (1 H, tt, $J_{2ax,3}$ = $J_{3,4ax}$ = 10.7 Hz, $J_{2eq,3}$ = $J_{3,4eq}$ = 4.3 Hz, H-3), 5.88 (1 H, d, $J_{8,9}$ = 3.4 Hz, H-8), 7.42–7.61, 8.01–8.12 (3 H, 2 H, OCOC$_6$H$_5$). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.66; H, 6.94.

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Preparation and Characterization of Cleavable Surfactants Based on a Silicon–Oxygen Bond

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Cleavable (destructible) surfactants are stable under certain conditions but are labile under other, generally mild conditions with respect to cleavage to nonsurfactant products.[1] Thus, they are appropriate for applications in which the presence of a surfactant, after its beneficial action, can lead to any one of several problems, including

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