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Prof. Akira Hosomi,
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

Supporting Information

Experimental Section

Boiling points listed in the section for compound data were determined with Kugelrohr distillation apparatus. For purification Merck silica gel 60 was used as an adsorbent. ^1H NMR spectra at 270 MHz and ^{13}C NMR spectra at 67.7 MHz were determined on a JEOL JNM-EX270 instrument as ppm from tetramethylsilane ($\delta = 0$) as a standard. Infrared spectra were measured with a Shimadzu IR-460 spectrophotometer. Mass spectra were measured (by EI method) on a Shimadzu GCMS-QP2000 and QP5000 instrument and high-resolution mass spectra were measured on JEOL JMS-GCMATE instrument. Microanalyses were performed by the Analysis Center of University of Tsukuba. Analyses agreed with the calculated values within 0.3%.

Solvents and Reagents. Unless otherwise specified, the following solvents and reagents (reagent grade) were used without further purification: palladium dichloride, mercuric dichloride, 1,2-diiodoethane (Tokyo Chemical Industry Co), samarium (Rare Metallic Co.), butyllithium/hexane solution (Kanto Chem. Co.), sodium hydride (60% dispersion in mineral oil), iodine, bromine, cinnamyl alcohol, ethyl acetate, and hexane. Triethylsilane was distilled prior to use. Aldehydes, methyl iodide, and diiodomethane were distilled under argon atmosphere and stored over molecular sieves (4A). *N,N,N',N'*-Tetramethylurea (TMU), hexamethylphosphoramide (HMPA) propargyl alcohol, and benzyl bromide were distilled over CaH_2 under argon atmosphere. Tetrahydrofuran, diethyl ether, and toluene were dried and distilled from benzophenone and sodium immediately prior to use under argon atmosphere.

Preparation of Iodotriethylsilane.¹ A 50 ml two-necked round bottom flask containing palladium dichloride (43 mg, 0.25 mmol), was fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon. The apparatus was purged with argon. Methyl iodide (1.78 g, 12.5 mmol) was added to the flask and the mixture was cooled to 0 °C. When triethylsilane (1.45 g, 12.5 mmol) was introduced to the flask, the reaction started vigorously accompanying with a generation of methane. After stirring at 0 °C for 2 h, iodosilane was directly distilled to a receiver containing a copper wire and stored in the dark. bp 191 °C/750 mmHg; ^1H NMR (CDCl_3) δ 1.0 (s, 15H).

Preparation of Iodomethyl Silyl Ethers 1 (in toluene). A 15 ml two-necked round bottom flask was fitted with a rubber septum and a reflux condenser with a

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Prof. Akira Hosomi,Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

three-way stopcock connected to a balloon filled with argon. The apparatus was purged with argon. Toluene (4.0 ml) and an aldehyde (0.968 g, 4.0 mmol) was added to the flask and the solution was cooled to -40 °C. To this flask, iodotriethylsilane (4.0 mmol) was introduced and the temperature was allowed to rise to room temperature. After stirring for further 3 h at room temperature, the conversion was checked by ¹H NMR measurement of a small portion under argon (disappearance of formyl proton). The toluene solution of **1** was obtained quantitatively and used in the samarium-mediated reactions.

1-Iodo-1-triethylsilyloxy-3-phenylpropane (1a). ¹H NMR (CDCl₃-toluene) δ 0.94 (q, *J* = 8.3 Hz, 6H), 1.34 (t, *J* = 8.3 Hz, 9H), 2.77-2.96 (m, 2H), 2.98-3.22 (m, 2H), 6.53 (dd, *J* = 5.9, 4.6 Hz, 1H), 7.38-7.71 (m, 5H).

1-Iodo-1-triethylsilyloxypropane (1b). ¹H NMR (CDCl₃-toluene) δ 0.77 (q, *J* = 8.3 Hz, 6H), 1.18 (t, *J* = 8.3 Hz, 9H), 1.22 (t, *J* = 7.3 Hz, 3H), 2.36-2.43 (m, 2H), 6.38 (t, *J* = 5.3 Hz, 1H).

1-Iodo-1-triethylsilyloxy-2-methylpropane (1c). ¹H NMR (CDCl₃-toluene) δ 0.69 (q, *J* = 7.6 Hz, 6H), 1.10 (t, *J* = 7.6 Hz, 9H), 1.20 (d, *J* = 6.6 Hz, 6H), 1.82 (m, 1H), 6.21 (d, *J* = 3.6 Hz, 1H).

1-Iodo-1-triethylsilyloxy-3-methylbutane (1d). ¹H NMR (CDCl₃-toluene) δ 0.65 (q, *J* = 7.9 Hz, 6H), 0.98-1.23 (m, 15H), 1.98 (m, 1H), 2.20-2.41 (m, 2H), 6.39 (dd, *J* = 8.3, 4.3 Hz, 1H).

Following dipolarophiles were prepared by ordinary Williamson synthesis using unsaturated alcohols.

(E)-1,4-Dimethoxy-2-butene (4c). (E)-1,4-dihydroxy-2-butene was prepared as following.² To the suspension of lithium aluminum hydride in THF (7.57 g, 200 mmol/150 ml) a solution of 1,4-dihydroxy-2-butyne in THF (8.6 g, 100 mmol/50 ml) was added at 0 °C under nitrogen. The mixture was stirred overnight with rising the temperature to room temperature. To the mixture, water (5 ml) was carefully added at 0 °C with stirring and subsequently ether (100 ml) and MgSO₄ were added. The resultant mixture was stirred for 1 h and filtered. Solvents of the filtrate were evaporated and the residue was distilled from CaH₂ (74%, 6.5 g). This diol was converted to diether.

42% (3.6 g); ¹H NMR (CDCl₃) δ 3.33 (s, 6H), 3.93 (dd, *J* = 3.0, 1.3 Hz, 4H), 5.79 (m, 2H); ¹³C NMR (CDCl₃) δ 57.9 (CH₃ x 2), 72.4 (CH₂ x 2), 129.4 (CH x 2).

(Z)-1,4-Dimethoxy-2-butene (4d). 45% (1.0 g). ¹H NMR (CDCl₃) δ 3.29 (s, 6H), 3.96 (dd, *J* = 4.7, 1.0 Hz, 4H), 5.67 (dt, *J* = 4.7, 1.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 58.0 (CH₃ x 2), 68.1 (CH₂ x 2), 129.3 (CH x 2). Anal. Calcd for C₆H₁₂O₂: C, 62.04; H, 10.41. Found: C, 61.95; H, 10.55.

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Prof. Akira Hosomi,Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

Cinnamyl Methyl Ether (4e). 99% (4.4 g). bp 80 °C/0.8 mmHg; ^1H NMR (CDCl_3) δ 3.34 (s, 3H), 4.04 (dd, $J = 5.9, 1.7$ Hz, 2H), 6.23 (dt, $J = 16.0, 5.9$ Hz, 1H), 6.56 (dd, $J = 16.0, 1.7$ Hz, 1H), 7.15-7.47 (m, 5H); ^{13}C NMR (CDCl_3) δ 58.0 (CH_3), 73.1 (CH_2), 125.9 (CH), 126.4 (CH x 2), 127.6 (CH), 128.5 (CH x 2), 132.4 (CH), 136.7 (quart.); IR (neat film) 3025 (s), 2880 (s), 1653 (w), 1595 (w), 1494 (s), 1465 (s), 1380 (s), 1190 (s), 1153 (w), 1117 (s), 1033 (m), 966 (s), 913 (m), 829 (w), 743 (s), 689 (s) cm^{-1} .

Benzyl Propargyl Ether (4g). 99% (14.5 g). ^1H NMR (CDCl_3) δ 2.48 (t, $J = 2.0$ Hz, 1H), 4.19 (d, $J = 2.0$ Hz, 2H), 4.60 (s, 2H), 7.24-7.47 (m, 5H); ^{13}C NMR (CDCl_3) δ 57.1 (CH_2), 71.5 (CH_2), 74.6 (quart.), 77.5 (CH), 127.9 (CH), 128.1 (CH x 2), 128.5 (CH x 2), 137.3 (quart.); IR (neat film) 3295 (s), 3070 (m), 2950 (s), 2115 (w), 1734 (w), 1495 (m), 1452 (s), 1355 (s), 1262 (m), 1206 (m), 1087 (s), 1027 (s), 936 (m), 912 (m), 740 (s), 696 (s) cm^{-1} .

Reaction of 1-Iodo-1-triethylsilyloxy-3-phenylpropane (1a) without Dipolarophiles.

Reaction Using SmI_2 Solution. Two sets of a 50 ml two-necked round bottom flask fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon were purged with argon. To one flask, a deep blue solution of SmI_2 in THF (0.1 M, 1.0 mmol, 10 ml) and *N,N,N',N'*-tetramethylurea (TMU, 0.5 ml) was added and the solution was refluxed for 30 min. To another flask, a solution of iodomethyl silyl ether **1a** in toluene (4.0 mmol/4.0 ml) was introduced. The refluxing red purple solution of SmI_2 in THF-TMU was transferred *via* double-ended needle to the solution of **1a** with stirring and the light yellow reaction mixture was further stirred for 5 min. The mixture was poured into saturated aqueous NH_4Cl , and after extraction with ether (20 ml x 3), drying over anhydrous Na_2SO_4 , and evaporation of solvents, a crude material was obtained. After removal of TMU by a short-path silica gel column, a product was subjected to a preparative TLC (hexane/ethyl acetate = 5:1) and pure **3a** was obtained (73%, 92 mg).

Reaction Using Sm-HgCl_2 (cat.). To a 50 ml two-necked round bottom flask containing samarium metal (316 mg, 2.1 mmol), fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon were purged with argon. Under reduced pressure this flask was flame-dried and after cooled down, argon was again introduced. HgCl_2 (109 mg, 0.4 mmol) was added to the flask in flashing argon. THF (5 ml) was added and the mixture was well stirred for 20 min. A solution of iodomethyl silyl ether **1a** in toluene (4.0 mmol/4.0 ml) was introduced to the white suspension at -78 °C and the temperature was allowed to rise to room temperature. The

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Prof. Akira Hosomi,Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

mixture was stirred for further 1 h. The resultant deep blue solution was poured into saturated aqueous NaHCO_3 and organics were extracted with ether (20 ml x 3). After drying over anhydrous Na_2SO_4 , evaporation of solvents, and purification by means of a preparative TLC (hexane/ethyl acetate = 5:1), pure oxirane **3a** was obtained (63%, 318 mg).

1,6-Diphenyl-3-hexene Oxide (3a). ^1H NMR (CDCl_3 , as a mixture of isomers, 82/18) δ 1.65-2.14 (m, 4H), 2.60-2.85 (m, 4H), 3.60-3.75 (m, 0.35H), 3.96 (dd, $J =$ Hz, 1.65H); ^{13}C NMR (CDCl_3) δ 32.2 (CH_2 x 2), 33.8 (CH_2 x 2), 58.4 (CH x 2), 126 (CH x 2), 128.4 (CH x 8), 141.3 (quart. x 2); IR (neat film) 2400 (m), 1599 (m), 1491 (m), 1213 (s), 1045 (m) cm^{-1} ; mass spectrum m/z (% relative intensity) 252 (M^+ , 18), 133 (43), 118 (74), 105 (45), 91 (100), 77 (28), 65 (46), 51 (30).

Reaction of 1-Iodo-1-triethylsilyloxy-3-phenylpropane (1a) with Aldehydes. A 50 ml two-necked round bottom flask fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon were purged with argon. To this flask, a deep blue solution of SmI_2 in THF (0.1 M, 1.2 mmol, 12 ml) and N,N,N',N' -tetramethylurea (TMU, 0.6 ml) was added and the solution was refluxed for 30 min. A mixture of a solution of iodomethyl silyl ether **1a** in toluene (0.5 mmol/0.5 ml) and an aldehyde prepared in advance at 0 $^\circ\text{C}$, was added to the refluxing red purple solution of SmI_2 in THF-TMU and the mixture was stirred for further 5 min. The light yellow mixture was poured into saturated aqueous NH_4Cl and extracted with ether (20 ml x 3). After drying over anhydrous Na_2SO_4 , evaporation of solvents, and removal of TMU by a short-path silica gel column, a pure 1,3-dioxolane **6** was obtained by column chromatography on florisil.

2,4-Di-(2-phenethyl)-5-ethyl-1,3-dioxolane (6a). bp 200 $^\circ\text{C}$ /0.5 mmHg; R_f = 0.13 (hexane/diethyl ether = 40:1). ^1H NMR (CDCl_3 , as a mixture of isomers, 83/17) δ 0.90 (t, $J = 7.5$ Hz, 3H), 1.46-2.12 (m, 6H), 2.53-2.88 (m, 4H), 3.44-3.64 (m, 2H), 3.90 (m, 1H, minor isomer), 4.00 (m, 1H, minor isomer), 4.96 (t, $J = 4.6$ Hz, 1H, major isomer), 5.12 (t, $J = 4.8$ Hz, 1H, minor isomer); ^{13}C NMR (CDCl_3 , major isomer) δ 10.2 (CH_3), 26.0 (CH_2), 30.0 (CH_2), 32.4 (CH_2), 35.0 (CH_2), 35.9 (CH_2), 80.0 (CH), 83.3 (CH), 102.4 (CH), 125.8 (CH), 125.9 (CH), 128.3 (CH x 2), 128.4 (CH x 4), 128.5 (CH x 2), 141.7 (quart.), 141.8 (quart.); IR (neat film) 1603 (m), 1495 (m), 1452 (s), 1135 (s), 1031 (s), 747 (s), 698 (s) cm^{-1} ; mass spectrum m/z (% relative intensity) major isomer; 310 (M^+ , 5), 232 (14), 205 (15), 159 (32), 117 (60), 91 (100), minor isomer; 310 (M^+ , 2), 232 (15), 205 (11), 159 (23), 117 (47), 91 (100).

2,4-Di-(2-phenethyl)-5-iso-propyl-1,3-dioxolane (6b). bp 200 $^\circ\text{C}$ /0.4 mmHg; R_f = 0.19 (hexane/diethyl ether = 30:1). ^1H NMR (CDCl_3) δ 0.83 (d, $J = 6.9$ Hz,

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5/9**Prof. Akira Hosomi,**Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

3H), 0.89 (d, $J = 6.6$ Hz, 3H), 1.58-1.99 (m, 5H), 2.48-2.89 (m, 4H), 3.33 (dd, $J = 6.3$, 5.8 Hz, 1H), 3.74 (ddd, $J = 9.2$, 5.8, 3.3 Hz, 1H), 4.98 (t, $J = 4.6$ Hz, 1H), 7.13-7.24 (m, 10H); ^{13}C NMR (CDCl_3) δ 18.4 (CH_3), 18.7 (CH_3), 30.1 (CH_2), 31.2 (CH), 31.4 (CH_2), 35.7 (CH_2), 35.9 (CH_2), 78.4 (CH), 87.9 (CH), 102.1 (CH), 125.8 (CH), 125.9 (CH), 128.4 ($\text{CH} \times 8$), 142.0 (quart. $\times 2$); IR (neat film) 1602 (m), 1495 (m), 1452 (m), 1387 (m), 1136 (s), 1050 (s), 934 (w), 747 (m), 697 (s) cm^{-1} ; mass spectrum m/z (% relative intensity) major isomer; 324 (M^+ , 2), 246 (12), 219 (12), 173 (15), 117 (61), 105 (15), 91 (100), 69 (42), 55 (17), 43 (30), minor isomer, 324 (M^+ , 4), 282 (5), 246 (5), 219 (9), 207 (15), 173 (14), 117 (15), 91 (100), 69 (36), 44 (96). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2$: C, 81.44; H, 8.70. Found: C, 81.34; H, 8.89.

2,4-Di-(2-phenethyl)-5-tert-butyl-1,3-dioxolane (6c). bp 190 $^\circ\text{C}/0.4$ mmHg; $R_f = 0.13$ (hexane/diethyl ether = 40:1). ^1H NMR (CDCl_3) δ 0.92 (s, 9H), 1.62-1.78 (m, 1H), 1.85-2.10 (m, 3H), 2.66-2.97 (m, 4H), 3.39 (d, $J = 5.3$ Hz, 1H), 3.92 (ddd, $J = 9.6$, 5.3, 3.3 Hz, 1H), 5.03 (t, $J = 4.6$ Hz, 0.6H), 7.18-7.37 (m, 10H); ^{13}C NMR (CDCl_3) δ 25.7 ($\text{CH}_3 \times 3$), 30.1 (CH_2), 32.6 (CH_2), 33.0 (quart.), 35.2 (CH_2), 36.5 (CH_2), 77.0 (CH), 89.7 (CH), 101.5 (CH), 125.8 ($\text{CH} \times 2$), 125.9 ($\text{CH} \times 2$), 128.4 ($\text{CH} \times 8$), 141.8 (quart. $\times 2$); IR (neat film) 1601 (m), 1495 (m), 1451 (s), 1394 (s), 1137 (s), 1030 (s), 934 (m), 747 (s), 697 (s) cm^{-1} ; mass spectrum m/z (% relative intensity) 338 (M^+ , 4), 260 (14), 233 (15), 118 (54), 91 (100), 57 (22). Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2$: C, 81.61; H, 8.93. Found: C, 81.61; H, 8.94.

Reaction of 1-Iodo-1-triethylsilyloxyalkane 1 with Carbon-Dipolarophiles (Sm (0) Conditions). A 50 ml two-necked round bottom flask containing samarium metal (316 mg, 2.1 mmol), fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon were purged with argon. Under reduced pressure this flask was flame-dried and after cooled down, argon was again introduced. HgCl_2 (109 mg, 0.4 mmol) was added to the flask in flashing argon. THF (5 ml) was added and the mixture was well stirred for 20 min. Dipolarophile (1.0 mmol) was added to the white suspension and the mixture was cooled to -78 $^\circ\text{C}$. A solution of iodomethyl silyl ether 1a in toluene (4.0 mmol/4.0 ml) was introduced and the temperature was allowed to rise to room temperature. The mixture was stirred for further 1 h. The resultant deep blue solution was poured into saturated aqueous NaHCO_3 and organics were extracted with ether (20 ml \times 3). After drying over anhydrous Na_2SO_4 , evaporation of solvents, and purification by means of a column chromatography on silica gel (hexane/ethyl acetate), a pure cycloadduct 5 was obtained.

Reaction of 1-Iodo-1-Triethylsilyloxyalkane 1 with Carbon-Dipolarophiles (SmI_2 -Sm (0) Conditions). A 50 ml two-necked round bottom

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6/9**Prof. Akira Hosomi,**Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

flask containing samarium metal (601 mg, 4.0 mmol), fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with argon were purged with argon. Under reduced pressure this flask was flame-dried and after cooled down, argon was again introduced. Iodine (1.016 g, 4.0 mmol) was added to the flask in flashing argon. THF (6 ml) was added and the mixture was refluxed for 5 h. At -78 °C, dipolarophile (1.0 mmol) and a solution of iodomethyl silyl ether **1** (4 mmol/4 ml) was added and then the temperature was immediately raised to room temperature by removing a cooling bath. The mixture was stirred for 3 h. The resultant deep blue solution was poured into saturated aqueous NaHCO₃ and organics were extracted with ether (20 ml x 3). After drying over anhydrous Na₂SO₄, evaporation of solvents, and purification by means of a column chromatography on silica gel (hexane/ethyl acetate), a pure cycloadduct **5** was obtained.

Cycloadducts **5** were isolated as an isomeric mixture in the yields shown in Table 1 and the major isomers could be purified and identified. Following compounds are the major isomer of cycloadducts, otherwise specified. The stereochemistries of these compounds were determined by ¹H-NOE experiments.

2,5-Di-(2-phenethyl)-tetrahydrofuran (5a). bp 200 °C/0.5 mmHg; *R_f* = 0.13 (hexane/diethyl ether = 40:1). ¹H NMR (CDCl₃) δ 1.40-2.08 (m, 8H), 2.47-2.90 (m, 4H), 3.90 (m, 2H), 7.00-7.32 (m, 10H); ¹³C NMR (CDCl₃) δ 32.0 (CH₂ x 2), 32.6 (CH₂ x 2), 37.7 (CH₂ x 2), 77.8 (CH x 2), 125.7 (CH x 2), 128.4 (CH x 8), 142.3 (quart. x 2).

2,5-Diethyl-3-octyltetrahydrofuran (5b). bp 110 °C/0.5 mmHg; *R_f* = 0.77 (hexane/diethyl ether = 10:1). ¹H NMR (CDCl₃) δ 0.84 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.7-0.9 (m, 3H), 1.0-1.8 (m, 20H), 2.15 (ddd, *J* = 12.2, 6.9, 5.3 Hz, 1H), 3.44 (dt, *J* = 7.6, 4.0 Hz, 1H), 3.79 (m, 1H); ¹³C NMR (CDCl₃) δ 10.3 (CH₃), 10.5 (CH₃), 14.6 (CH₃), 22.8 (CH₂), 27.7 (CH₂), 28.5 (CH₂), 29.0 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 29.9 (CH₂), 31.9 (CH₂), 33.5 (CH₂), 39.2 (CH₂), 45.0 (CH), 79.5 (CH), 85.2 (CH); IR (neat film) 2930 (s), 1461 (m), 1377 (w), 1119 (w), 989 (w), 920 (w), 721 (w) cm⁻¹; mass spectrum *m/z* (% relative intensity) 211 (M⁺-Et, 36), 193 (4), 141 (10), 109 (9), 111 (6), 97 (15), 95 (12), 83 (17), 81 (17), 69 (32), 56 (32), 55 (100), 43 (58), 41 (99); HRMS (M⁺-Et) calcd for C₁₄H₂₇O 211.2062, found 211.2062.

2(S*),5(S*)-Diethyl-3(S*),4(S*)-di-(methoxymethyl)tetrahydrofuran (5c). bp 100 °C/0.6 mmHg; *R_f* = 0.54 (hexane/diethyl ether = 10:1). ¹H NMR (CDCl₃) δ 0.95 (t, *J* = 7.4 Hz, 6H), 1.44-1.67 (m, 4H), 1.83 (ddd, *J* = 6.3, 4.3, 4.0 Hz, 1H), 3.32 (s, 6H), 3.30-3.44 (m, 4H; changed to 3.36, d, *J* = 9.5 Hz, 2H and 3.39, d, *J* = 9.5 Hz, 2H, by irr. at 1.83), 3.65 (m, 2H, coalescing to dd, *J* = 7.3, 4.6 Hz by irr. at 1.83); ¹³C NMR (CDCl₃) δ 10.4 (CH₃ x 2), 28.0 (CH₃ x 2), 48.2 (CH x 2), 58.9 (CH₃ x 2), 74.9 (CH₂ x 2), 82.2 (CH x 2); IR (neat film) 2965 (s), 1460 (m), 1381 (w), 1194 (w), 1116

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Prof. Akira Hosomi,Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

(s), 988 (m), 957 (m) cm^{-1} ; mass spectrum m/z (% relative intensity) 187 (M^+ -Et, 2), 155 (35), 123 (20), 97 (4), 95 (21), 71 (10), 67 (18), 57 (21), 55 (22), 45 (100), 43 (19), 41 (39).

2(S*),5(S*)-Diethyl-3(S*),4(R*)-di-(methoxymethyl)tetrahydrofuran

(5d). bp 100 °C/0.6 mmHg; R_f = 0.54 (hexane/diethyl ether = 10:1). ^1H NMR (CDCl_3) δ 0.90 (t, J = 7.4 Hz, 6H), 1.30-1.69 (m, 4H), 2.15-2.35 (m, 2H), 3.30 (s, 3H), 3.33 (s, 3H), 3.31-3.38 (m, 1H), 3.41 (d, J = 5.3 Hz, 2H), 3.50 (dd, J = 9.2, 7.3 Hz, 1H), 3.65 (dt, J = 7.6, 4.3 Hz, 1H), 3.85 (ddd, J = 7.9, 5.6, 5.3 Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.5 (CH_3), 11.1 (CH_3), 23.7 (CH_2), 28.8 (CH_2), 43.3 (CH), 47.2 (CH), 58.7 (CH_3), 58.8 (CH_3), 69.1 (CH_2), 72.1 (CH_2), 81.4 (CH), 81.9 (CH); IR (neat film) 2930 (s), 1460 (s), 1393 (m), 1197 (m), 1108 (m), 989 (s), 961 (m), 861 (w), 803 (w) cm^{-1} ; mass spectrum m/z (% relative intensity) 187 (M^+ -Et, 3), 155 (7), 123 (5), 95 (8), 67 (11), 55 (13), 45 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_3$: C, 66.63; H, 11.18. Found: C, 66.35; H, 10.99.

2,5-Diethyl-3-methoxymethyl-4-phenyltetrahydrofuran (5e-major isomer). bp 130 °C/1.0 mmHg; R_f = 0.4 (hexane/diethyl ether = 10:1). ^1H NMR (CDCl_3) δ 0.90 (t, J = 7.4 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H), 1.45-1.82 (m, 4H), 2.27 (m, 1H; coalescing to ddd, J = 9.9, 6.1, 4.5 Hz by irr. at 3.90), 2.73 (dd, J = 9.9, 9.2 Hz, 1H), 3.34 (s, 3H), 3.37 (m, 1H; coalescing to d, J = 10.6 Hz by irr. at 2.27), 3.39 (m, 1H; coalescing to d, J = 10.6 Hz by irr. at 2.27), 3.90 (m, 2H), 7.18-7.38 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.4 (CH_3 x 2), 20.7, (CH_2), 28.4 (CH_2), 53.7 (CH), 54.7 (CH), 58.9 (CH_3), 73.0 (CH_2), 82.9 (CH), 85.5 (CH), 126.6 (CH), 128.0 (CH x 2), 128.7 (CH x 2), 140.9 (quart.); IR (neat film) 1601 (w), 1495 (m), 1455 (s), 1380 (s), 1191 (w), 1110 (s), 987 (s), 753 (s), 700 (s) cm^{-1} ; mass spectrum m/z (% relative intensity) 217 (M^+ -Et, 28), 187 (25), 140 (14), 109 (75), 91 (100), 81 (36), 65 (45), 57 (55), 53 (25).

2,5-Diethyl-3-methoxymethyl-4-phenyltetrahydrofuran (5e-minor isomer). R_f = 0.4 (hexane/diethyl ether = 10:1); ^1H NMR (CDCl_3) δ 0.90 (t, J = 7.4 Hz, 3H), 1.05 (t, J = 7.3 Hz, 3H), 1.40-1.70 (m, 4H), 2.65 (m, 2H), 3.23 (s, 3H), 3.33-3.40 (m, 1H), 3.41 (dd, J = 9.2, 8.6 Hz, 1H), 3.87 (m, 1H), 4.18 (m, 1H), 7.12-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.9 (CH_3), 11.6 (CH_3), 24.5 (CH_2), 27.9 (CH_2), 51.1 (CH), 54.1 (CH), 59.1 (CH_3), 72.2 (CH_2), 82.4 (CH), 87.3 (CH), 127.1 (CH), 128.4 (CH x 2), 129.1 (CH x 2), 142.0 (quart.). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$: C, 77.38; H, 9.74. Found: C, 77.31; H, 9.86.

2,5-Diethyl-3-phenyl-2,5-dihydrofuran (5f). bp 90 °C/0.5 mmHg; R_f = 0.89 (hexane/diethyl ether = 10:1). ^1H NMR (CDCl_3) δ 0.82 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H), 1.48-1.85 (m, 4H), 4.86 (m, 1H), 5.29 (m, 1H), 6.00 (brs, 1H), 7.09-7.35 (m, 5H); ^{13}C NMR (CDCl_3) δ 8.7 (CH_3), 9.3 (CH_3), 27.2 (CH_2), 29.2 (CH_2), 86.1

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Prof. Akira Hosomi,Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

(CH), 86.9 (CH), 125.3 (CH), 126.4 (CH x 2), 127.7 (CH), 128.5 (CH x 2), 133.6 (quart.), 141.7 (quart.); IR (neat film) 2935 (s), 1599 (w), 1494 (m), 1457 (m), 1379 (w), 1348 (w), 1107 (m), 1074 (m), 755 (s), 691 (s) cm^{-1} ; mass spectrum m/z (% relative intensity) 202 (M^+ , 11), 173 (95), 145 (45), 128 (22), 115 (37), 91 (40), 77 (25), 57 (100), 43 (65); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1358, found 202.1364.

2,5-Diethyl-3-benzyloxymethyl-2,5-dihydrofuran (5g). bp 130 °C/0.4 mmHg; R_f = 0.4 (hexane/ethyl acetate = 10:1). ^1H NMR (CDCl_3) δ 0.84 (t, J = 7.6 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H), 1.36-1.66 (m, 4H), 3.98 (s, 2H), 4.42 (d, J = 11.9 Hz, 1H), 4.48 (d, J = 11.9 Hz, 1H), 4.73 (m, 2H), 5.67 (s, 1H), 7.17-7.27 (m, 5H); ^{13}C NMR (CDCl_3) δ 8.6 (CH_3), 9.2 (CH_3), 27.0 (CH_2), 29.0 (CH_2), 65.6 (CH_2), 72.2 (CH_2), 85.9 (CH), 86.2 (CH), 126.6 (CH), 127.8 (CH x 3), 128.3 (CH x 2), 137.9 (quart.), 139.5 (quart.); IR (neat film) 1496 (w), 1452 (s), 1378 (m), 1197 (w), 1095 (s), 1013 (m), 916 (w), 875 (w), 735 (s), 695 (s) cm^{-1} .

2,5-Di-*iso*-propyl-3-methoxymethyl-4-phenyltetrahydrofuran (5h). bp 120 °C/2.0 mmHg; R_f = 0.42 (hexane/ethyl acetate = 10:1). ^1H NMR (CDCl_3) δ 0.80 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H), 1.70-2.03 (m, 2H), 2.89 (dd, J = 9.2, 8.9 Hz, 1H), 2.28 (m, 1H), 3.16 (s, 3H), 3.26 (m, 1H, coalescing to d, J = 5.6 Hz by irr. at 2.28), 3.55 (dd, J = 6.6, 5.9 Hz, 1H), 3.68 (dd, J = 8.9, 5.6 Hz, 1H), 7.17-7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.8 (CH_3), 18.2 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 31.9 (CH), 32.1 (CH), 52.8 (CH), 52.9 (CH), 58.8 (CH_3), 73.5 (CH_2), 85.7 (CH), 89.0 (CH), 126.0 (CH), 127.8 (CH x 2), 128.5 (CH x 2), 142.6 (quart.).

2,5-Di-*iso*-propyl-3-(*E*)-methoxymethylidenetetrahydrofuran (5i). ^1H NMR (CDCl_3) δ 0.84 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 1.66 (m, 2H), 2.31 (ddd, J = 15.8, 6.6, 2.3 Hz, 1H; coalescing to dd, J = 15.8, 6.6 Hz by irr. at 4.10), 2.48 (ddt, J = 15.8, 7.3, 1.7 Hz, 1H; coalescing to ddd, J = 15.8, 7.3, 2.1 Hz by irr. at 4.10), 3.59 (s, 3H), 3.72 (q, J = 7.3 Hz, 1H), 4.11 (brd, J = 6.0 Hz, 1H), 5.87 (brs, 1H); ^{13}C NMR (CDCl_3) δ 16.7 (CH_3), 17.4 (CH_3), 18.7 (CH_3), 19.9 (CH_3), 31.0 (CH_2), 33.0 (CH), 33.2 (CH), 59.6 (CH_3), 83.5 (CH), 83.8 (CH), 119.1 (quart.), 139.1 (CH); mass spectrum m/z (% relative intensity) 198 (M^+ , 2), 155 (86), 137 (20), 123 (58), 99 (100), 95 (62), 81 (45), 71 (52), 55 (69), 43 (95).

2,5-Di-*iso*-propyl-3-benzyloxymethyl-2,5-dihydrofuran (5j). bp 110 °C/0.4 mmHg; R_f = 0.6 (hexane/ethyl acetate = 10:1). ^1H NMR (CDCl_3) δ 0.81 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.81 (m, 2H), 4.06 (s, 2H), 4.49 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 12.1 Hz, 1H), 4.61 (m, 1H), 4.73 (m, 1H), 5.77 (brs, 1H), 7.26-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ

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Prof. Akira Hosomi,

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan;
phone: +81-298-53-4237; facsimile: +81-298-53-6503;
e-mail: hosomi@staff.chem.tsukuba.ac.jp

15.0 (CH₃), 17.5 (CH₃), 18.3 (CH₃), 14.4 (CH₃), 31.7 (CH), 33.6 (CH), 65.9 (CH₂), 72.2 (CH₂), 89.0 (CH), 90.9 (CH), 125.2 (CH), 127.6 (CH x 3), 128.5 (CH x 2), 138.0 (quart.), 139.8 (quart.); mass spectrum *m/z* (% relative intensity) 231 (M⁺-*i*-Pr, 15), 201 (12), 123 (25), 91 (100), 43 (42). Anal. Calcd for C₁₈H₂₆O₂: C, 78.79; H, 9.55. Found: C, 78.49; H, 9.71.

2,5-Di-*iso*-butyl-3-benzyloxymethyl-2,5-dihydrofuran (5k). *R*_f = 0.80 (hexane/ethyl acetate = 10:1). ¹H NMR (CDCl₃) δ 0.93 (d, *J* = 6.6 Hz, 12H), 1.41-1.50 (m, 3H), 1.57 (dd, *J* = 13.0, 6.6 Hz, 1H), 1.66-1.92(m, 2H), 3.95 (s, 2H), 4.38 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.73 (m, 2H), 5.82 (m, 1H; coalescing to s by irr. at 4.73), 7.21-7.38 (m, 5H); ¹³C NMR (CDCl₃) δ 22.0 (CH₃), 22.9 (CH₃), 23.1 (CH₃), 23.9 (CH₃), 25.0 (CH), 25.2 (CH), 43.7 (CH₂), 45.3 (CH₂), 65.7 (CH₂), 72.3 (CH₂), 82.9 (CH), 83.0 (CH), 127.0 (CH), 127.7 (CH x 2), 128.5 (CH x 3), 138.1 (quart.), 140.6 (quart.); mass spectrum *m/z* (% relative intensity) 302 (M⁺, 0.08), 245 (M⁺-*i*-Bu, 10), 215 (16), 196 (3), 137 (26), 91 (100), 81 (11), 57 (22), 41 (47).

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