Supporting Information

Triethylborane-induced Radical Reactions with Gallium Hydride Reagent $HGaCl_2$

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Instrumentation and Materials

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Gallium trichloride and triethylborane were purchased from Aldrich Chemicals and were diluted to prepare a 1.0 M hexane solution to handle easily. Red-Al® (70wt% in toluene) was obtained from Nacalai Tesque Inc., and was diluted with toluene to prepare a 2.0 M solution. These solutions were stored strictly under argon. Halo acetals were prepared according to the literature (ref. 14).

Experimental Section

The reaction was performed in a reaction flask equipped with a toy balloon that was filled with argon unless otherwise noted. Oxygen, which is necessary to produce an ethyl radical from triethylborane, could penetrate the balloon easily. Additional oxygen was not necessary.

Procedure for Reduction of Alkyl Halide.

Gallium trichloride in hexane (1.0 M solution prepared in advance, 2.0 mL, 2.0 mmol) was placed in a reaction flask under argon and was diluted with 3 mL of THF. Sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al, 2.0 M toluene solution, 0.50 mL, 1.0 mmol) was then added to the solution at 0 ˚C and the resulting mixture was stirred for 30 min. 1-Iodododecane (296 mg, 1.0 mmol in 2 mL of THF) and triethylborane (1.0 M hexane solution, 0.10 mL, 0.10 mmol) were sequentially added. After being stirred for 4 h at 0 ˚C, the reaction was quenched with 1 M hydrochloric acid (20 mL), and the product was extracted with hexane (20 mL × 3). Combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Silica gel column purification afforded 156 mg of dodecane in 92% yield. Reduction of bromide was performed with 1.0 mmol of triethylborane.

Typical Procedure for Cyclization of Halo Acetal.

Halo acetal **1a** (296 mg, 1.0 mmol) in 2 mL of THF was added to a solution of the gallium hydride (1.5 mmol) prepared as above, and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) was added. After being stirred for 5 h at 0 ˚C, the mixture was poured into 1 M HCl and was stirred for 15 min. Extraction with hexane/ethyl acetate (10/1 = v/v%, 20 mL × 3) followed by silica gel column purification afforded **2a** (146 mg) in 86% yield. Diastereomer ratio was determined by the ^{1}H NMR experiment of the product, judging from the integrations of the proper protons.

Radical Cyclization with a Catalytic Amount of $GaCl_3$.

A mixture of gallium trichloride (1.0 M hexane solution, 0.20 mL, 0.20 mmol), **1a** (296 mg, 1.0 mmol), and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) in THF (5 mL) was placed in a 50-mL reaction flask. Red-Al (0.75 mL, 1.5 mmol) was added to the reaction mixture over 2 h with a syringe pump at 0 ˚C. After the slow addition was completed, the whole mixture was stirred for 1 h. Quenching the reaction with hydrochloric acid followed by extraction with hexane/ethyl acetate (10/1=v/v%, 20 mL × 3), concentration, and silica gel column purification yielded 134 mg of **2a** (0.79 mmol, 79%) as a colorless oil.

Characterization Data

7-Isopropyl-2,9-dioxabicyclo[4.3.0]nonane (2a, 70/30 Isomeric Mixture): Faster moving band, R_f = 0.53 (hexane/ethyl acetate = 3/1): IR (neat) 2936, 1467, 1402, 1253, 1142, 1114, 1087, 1031, 1000, 950, 898 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 1.27–1.43 (m, 1H), 1.50–1.74 (m, 4H), 1.85–1.95 (m, 2H), 3.64–3.79 (m, 3H), 3.92 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.27 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.74, 20.88, 21.65, 23.21, 26.22, 35.67, 48.90, 60.70, 68.99, 102.11. Found: C, 70.52; H, 10.39%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%. **Slower moving band, R_f = 0.47 (hexane/ethyl acetate = 3/1)**: IR (neat) 3510, 2876, 1468, 1387, 1369, 1221, 1149, 1115, 1089, 1061, 1029, 949, 894, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 1.29–1.39 (m, 1H), 1.58–1.75 (m, 2H), 1.75–1.92 (m, 3H), 2.08 (dddd, *J* = 7.2, 8.1, 8.1, 8.7 Hz, 1H), 3.41 (ddd, *J* = 2.4, 11.4, 11.4 Hz, 1H), 3.66 (dd, *J* = 8.1, 8.4 Hz, 1H), 3.86 (ddd, *J* = 3.3, 3.9, 11.4 Hz, 1H), 4.16 (dd, *J* = 8.4, 8.7 Hz, 1H), 4.97 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.37, 20.65, 21.36, 23.43, 29.98, 41.27, 44.31, 64.26, 71.03, 102.50. Found: C, 70.32; H, 10.39%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

7-Butyl-2,9-dioxabicyclo[4.3.0]nonane (2c, 84/16 Isomeric Mixture): IR (neat): 2924, 2856, 1724, 1467, 1403, 1253, 1146, 1090, 1023, 949, 902, 870 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 6.9 Hz, 3H), 1.10–1.45 (m, 7H), 1.54–1.98 (m, 4H), 2.25–2.37 (m, 1H), 3.42 (ddd, *J* = 11.4 Hz, 11.4 Hz, 1.8 Hz, 0.16H), 3.54 (dd, *J* = 8.4 Hz, 8.4 Hz, 0.16H), 3.60–3.69 (m, 0.84 × 2H), 3.70–3.80 (m, 0.84H), 3.80–3.94 (m, 0.16H), 3.95 (dd, *J* = 8.1 Hz, 8.1 Hz, 0.84H), 4.28 (dd, *J* = 8.4 Hz, 8.4 Hz, 0.16H), 5.00 (d, *J* = 3.6 Hz, 0.16H), 5.28 (d, *J* = 3.6 Hz, 0.84H); ^{13}C NMR ($CDCl_3$): For major isomer: δ = 13.83, 19.05, 22.74, 23.12, 26.55, 30.35, 36.41, 40.91, 60.89, 70.12, 102.06. For minor isomer: δ = 13.83, 20.61, 22.30, 22.78, 30.62, 32.32, 37.74, 44.06, 64.42, 74.26, 102.06. Found: C, 71.57; H, 11.21%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%.

7-Methyl-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (2e, 56/44 Isomeric Mixture): **Faster moving**

band, R_f = 0.56 (hexane/ethyl acetate = 5/1): IR (neat) 3440, 2928, 2870, 1648, 1459, 1402, 1380, 1251, 1146, 1114, 1073, 994, 965, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 1.18–1.70 (m, 12H), 1.86–2.02 (m, 2H), 3.59 (ddt, *J* = 3.6, 11.1, 1.5 Hz, 1H), 3.68–3.79 (m, 2H), 5.25 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.48, 13.90, 20.06, 22.49, 23.16, 25.84, 31.94, 35.02, 39.02, 40.70, 61.00, 82.70, 100.90. Found: C, 73.33; H, 11.58%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%. **Slower moving band, R_f = 0.47 (hexane/ethyl acetate = 5/1)**: IR (neat) 3500, 2926, 1458, 1377, 1340, 1221, 1156, 1128, 1097, 1043, 980, 943, 900, 864, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.3 Hz, 3H), 1.21–1.40 (m, 6H), 1.46–1.73 (m, 5H), 1.74–1.83 (m, 2H), 1.92 (ddq, *J* = 8.1, 11.9, 6.3 Hz, 1H), 3.36 (ddd, *J* = 2.1, 11.7, 11.7 Hz, 1H), 3.54 (dt, *J* = 8.9, 6.0 Hz, 1H), 3.85 (ddd, *J* = 2.1, 2.1, 11.7 Hz, 1H), 4.92 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 15.11, 20.59, 21.72, 22.52, 26.13, 31.83, 36.09, 37.58, 46.21, 64.45, 87.84, 101.52. Found: C, 73.68; H, 11.35%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

2-Butoxy-4-butyltetrahydrofuran (2g, 84/16 Isomeric Mixture): Bp 100 ˚C (3 torr); IR (neat) 2862, 1466, 1346, 1265, 1194, 1013, 934, 829, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 0.16 × 6H), 0.92 (t, *J* = 7.2 Hz, 0.84 × 6H), 1.17–1.60 (m, 11H), 1.99–2.44 (m, 2H), 3.31–3.40 (m, 0.16 × 1H), 3.36 (dt, *J* = 6.6, 9.3 Hz, 0.84 × 1H), 3.45 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.52–3.62 (m, 0.16 × 1H), 3.67 (dt, *J* = 6.6, 9.3 Hz, 0.84 × 1H), 3.93 (dd, *J* = 8.1, 8.1 Hz, 0.84 × 1H), 4.04 (dd, *J* = 8.1, 8.1 Hz, 0.16 × 1H), 5.07–5.10 (m, 0.16 × 1H), 5.09 (dd, 5.7, 3.3 Hz, 0.84 × 1H); ^{13}C NMR ($CDCl_3$) For major isomer, δ 13.68, 13.82, 19.23, 22.64, 30.75, 31.75, 32.65, 38.51, 38.99, 67.31, 71.77, 104.51. Found: C, 71.68; H, 12.35%. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

2-Butoxy-4-methyl-5-pentyltetrahydrofuran (2i, 50/50 Isomeric Mixture): Bp 110 ˚C (1 Torr); IR (neat) 2954, 2928, 2868, 1460, 1379, 1344, 1098, 994, 921, 901 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.0 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.0 Hz, 0.5H), 1.04 (d, *J* = 6.6 Hz, 1.5H), 1.22–1.62 (m, 13H), 1.74 (dtq, *J* = 6.6, 8.1, 9.2 Hz, 0.5H), 2.05 (dd, *J* = 6.6, 11.7 Hz, 0.5H), 2.00–2.18 (m,

0.5H), 2.32 (ddd, *J* = 5.7, 9.2, 13.2 Hz, 0.5H), 3.33 (dt, *J* = 6.5, 9.3 Hz, 0.5H), 3.38 (dt, *J* = 6.6, 9.6 Hz, 0.5H), 3.46–3.56 (m, 1H), 3.68 (dt, *J* = 6.9, 9.3 Hz, 0.5H), 3.69 (dt, *J* = 6.8, 9.6 Hz, 0.5H), 5.00 (d, *J* = 5.1 Hz, 0.5H), 5.07 (dd, *J* = 3.0, 5.7 Hz, 0.5H); ^{13}C NMR ($CDCl_3$) δ 13.75, 13.93, 13.97, 17.09, 17.17, 19.27, 19.33, 22.53, 25.95, 25.99, 31.77, 31.82, 31.90, 31.95, 33.68, 35.84, 36.81, 38.16, 41.31, 41.88, 66.57, 67.26, 83.91, 86.90, 103.24, 103.40. Found: C, 73.40; H, 12.30%. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36%.