

Supporting Information

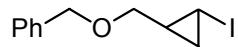
Stereoselective Iodocyclopropanation of Terminal Alkenes with Iodoform, Chromium(II) Chloride, and TEEDA

Kazuhiko Takai,* Shota Toshikawa, Atsushi Inoue and Ryo Kokumai

*Department of Applied Chemistry, Faculty of Engineering,
Okayama University, Tsushima, Okayama 700-8530, Japan*

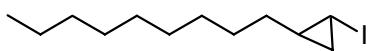
Experimental Conditions: Dry, oxygen-free tetrahydrofuran (THF) was purchased from Kanto Chemicals, Co. Column chromatography was performed with silica gel (200 mesh). Distillation of small amounts of the products was performed with a Büchi Kugelrohr, and boiling points were indicated by an air bath temperature without correction. FT-IR spectra were obtained on a Nicolet Protégé 460 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 instrument. Chemical shifts were expressed in ppm downfield from internal tetramethylsilane using a δ scale. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

General Procedure: To a mixture of CrCl_2 (0.49 g, 4.0 mmol) in dry, oxygen-free THF (5 mL) was added TEEDA (0.85 mL, 4.0 mmol) at 25 °C. The color of the mixture turned from greenish white to purple. After stirring for 15 min at 25 °C, a solution of an alkene (1.0 mmol) in THF (2 mL) was added to the mixture at 25 °C. A solution of iodoform (0.59 g, 1.5 mmol) in THF (3 mL) was added dropwise to the mixture at 25 °C over a period of 5 min. The color of the mixture turned to brown and then black. After stirring for an appropriate time shown in Table 1 at 25 °C, the reaction mixture was poured into aqueous hydrochloric acid (1 M, 15 mL). The mixture was extracted with ether (3 x 20 mL), and organic extracts were washed with aqueous sodium thiosulfate (2 x 20 mL), dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel gave the desired iodocyclopropane.

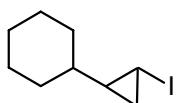


***trans*-(2-Iodocyclopropyl)methyl benzyl ether (**4**):**¹ IR (neat): 3029, 2856, 1496, 1453, 1253, 1212, 1095, 1077, 1039, 737 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.98-1.02 (m, 2H), 1.49-1.57 (m, 1H), 2.23-2.27 (m, 1H), 3.35 (dd, J = 10.5, 6.6 Hz, 1H), 3.44 (dd, J = 10.5, 6.3 Hz, 1H),

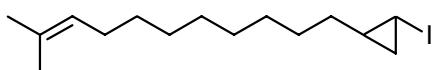
4.51 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 7.26-7.38 (m, 5H); $^{13}\text{CNMR}$ (CDCl_3): δ - 17.6, 14.6, 22.9, 71.6, 72.6, 127.7, 127.7, 128.4, 138.0.



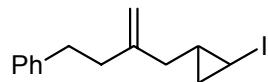
trans-1-iodo-2-nonylcyclopropane: Bp 110 °C (bath temp, 0.9 Torr); IR (neat): 2955, 2924, 2853, 1465, 1441, 1378, 1216, 1194, 1076, 1034 cm^{-1} ; $^1\text{HNMR}$ (CDCl_3): δ 0.78 (ddd, $J = 7.8, 4.0, 4.0$ Hz, 1H), 0.87-0.91 (m, 4H), 1.11-1.19 (m, 1H), 1.24-1.32 (m, 14H), 1.35-1.42 (m, 2H), 2.07 (ddd, $J = 7.8, 4.0, 4.0$ Hz, 1H); $^{13}\text{CNMR}$ (CDCl_3): δ -14.6, 14.1, 16.6, 22.7, 23.7, 28.7, 29.3, 29.4, 29.6, 29.6, 31.9, 33.5. Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{I}$: C, 48.99; H, 7.88. Found: C, 49.27; H, 7.75.



trans-(2-Iodocyclopropyl)cyclohexane: Bp 57 °C (bath temp, 0.6 Torr); IR (neat): 2922, 2851, 1448, 1241, 1208, 1192, 1063, 1035, 936 cm^{-1} ; $^1\text{HNMR}$ (CDCl_3): δ 0.58-0.68 (m, 1H), 0.79-0.88 (m, 2H), 0.98-1.08 (m, 2H), 1.12-1.20 (m, 4H), 1.60-1.74 (m, 4H), 1.78-1.85 (m, 1H), 2.13 (ddd, $J = 7.3, 4.2, 4.2$ Hz, 1H); $^{13}\text{CNMR}$ (CDCl_3): δ -16.4, 15.3, 26.0, 26.0, 26.3, 30.0, 32.0, 32.2, 42.2. Anal. Calcd for $\text{C}_9\text{H}_{15}\text{I}$: C, 43.22; H, 6.04. Found: C, 43.35; H, 5.90.

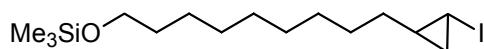


trans-1-Iodo-2-(10-methyl-9-undecenyl)cyclopropane (5): IR (neat): 2993, 2965, 2853, 1455, 1441, 1376, 1217, 1192, 1034 cm^{-1} ; $^1\text{HNMR}$ (CDCl_3): δ 0.78 (ddd, $J = 7.6, 6.2, 6.1$ Hz, 1H), 0.89 (ddd, $J = 9.0, 6.0, 4.5$ Hz, 1H), 1.08-1.19 (m, 1H), 1.24-1.32 (m, 12H), 1.33-1.41 (m, 2H), 1.60 (s, 3H), 1.69 (s, 3H), 1.92-2.00 (m, 2H), 2.07 (ddd, $J = 7.8, 3.9, 3.9$ Hz, 1H), 5.11 (t, $J = 7.3$ Hz, 1H); $^{13}\text{CNMR}$ (CDCl_3): δ -14.7, 16.5, 17.7, 23.7, 25.7, 28.0, 28.7, 29.3, 29.3, 29.5, 29.5, 29.9, 33.5, 124.9, 131.1. Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{I}$: C, 53.90; H, 8.14. Found: C, 53.98; H, 7.93.

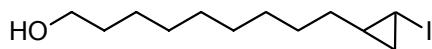


trans-[3-(2-Iodocyclopropylmethyl)-3-butenyl]benzene (6): IR (neat): 3026, 2924, 2857, 1645, 1496, 1453, 1437, 1214, 1189, 1035, 894, 747, 698 cm^{-1} ; $^1\text{HNMR}$ (CDCl_3): δ 0.84 (ddd, $J = 7.8, 6.1, 6.1$ Hz, 1H), 0.96 (ddd, $J = 9.1, 4.6, 3.1$ Hz, 1H), 1.24-1.34 (m, 1H), 1.96 (dd, $J = 15.9, 7.5$ Hz, 1H), 2.04-2.12 (m, 2H), 2.34 (dd, $J = 8.4, 7.6$ Hz, 2H), 2.74 (dd, $J = 8.4, 7.6$ Hz, 2H), 4.82 (s, 1H), 4.89 (s, 1H), 7.15-7.29 (m, 5H); $^{13}\text{CNMR}$ (CDCl_3): δ -14.7, 16.6,

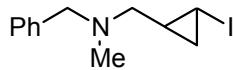
22.0, 26.9, 34.4, 38.0, 40.2, 110.4, 125.8, 128.3, 142.0, 147.4. Anal. Calcd for C₁₄H₁₇I: C, 53.86; H, 5.49. Found: C, 53.98; H, 5.51.



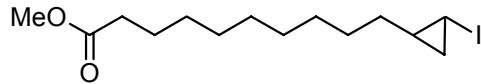
trans-[9-(2-Iodocyclopropyl)nonyloxy]trimethylsilane: IR (neat): 2926, 2854, 1259, 1250, 1097, 873, 841, 747 cm⁻¹; ¹HNMR (CDCl₃): δ 0.11 (s, 9H), 0.78 (ddd, J = 7.5, 6.0, 6.0 Hz, 1H), 0.89 (ddd, J = 9.0, 6.0, 4.5 Hz, 1H), 1.10-1.18 (m, 1H), 1.25-1.35 (m, 12H), 1.35-1.42 (m, 2H), 1.48-1.56 (m, 2H), 2.07 (ddd, J = 7.7, 4.2, 3.8 Hz, 1H), 3.57 (t, J = 6.8 Hz, 2H); ¹³CNMR (CDCl₃): δ -14.7, -0.5, 16.5, 23.7, 25.8, 28.7, 29.3, 29.4, 29.5, 29.5, 32.7, 33.5, 62.7. Anal. Calcd for C₁₅H₃₁IOSi: C, 47.11; H, 8.17. Found: C, 47.29; H, 8.31.



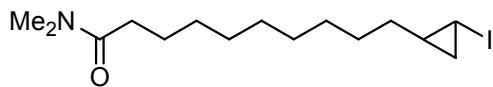
trans-9-(2-Iodocyclopropyl)nonan-1-ol: IR (neat): 3338, 2924, 2853, 1464, 1439, 1218, 1192, 1057, 1034 cm⁻¹; ¹HNMR (CDCl₃): δ 0.78 (ddd, J = 7.5, 6.0, 6.0 Hz, 1H), 0.89 (ddd, J = 9.0, 6.0, 4.2 Hz, 1H), 1.11-1.18 (m, 1H), 1.19-1.23 (m, 1H), 1.26-1.39 (m, 14H), 1.57 (tt, J = 6.9, 6.9 Hz, 2H), 2.07 (ddd, J = 7.7, 3.9, 3.9 Hz, 1H), 3.64 (q, J = 6.1 Hz, 2H); ¹³CNMR (CDCl₃): δ -14.7, 16.5, 23.7, 25.7, 28.7, 29.3, 29.3, 29.4, 29.5, 32.8, 33.5, 63.0. Silylation of the alcohol afforded the above compound.



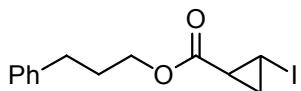
trans-Benzyl-(2-iodocyclopropylmethyl)methylamine: IR (neat): 2788, 1453, 1365, 1216, 1193, 1075, 1039, 1025, 739, 699 cm⁻¹; ¹HNMR (CDCl₃): δ 0.79 (ddd, J = 7.7, 6.2, 6.2 Hz, 1H), 0.93 (ddd, J = 9.3, 6.3, 4.5 Hz, 1H), 1.31-1.36 (m, 1H), 2.04-2.13 (m, 2H), 2.24 (s, 3H), 2.48 (dd, J = 12.9, 5.7 Hz, 1H), 3.45 (d, J = 12.9 Hz, 1H), 3.67 (d, J = 13.2 Hz, 1H), 7.19-7.29 (m, 5H); ¹³CNMR (CDCl₃): δ -15.1, 15.3, 21.5, 42.4, 60.6, 62.1, 127.0, 128.3, 129.0, 138.9. Anal. Calcd for C₁₂H₁₆IN: C, 47.86; H, 5.35. Found: C, 47.88; H, 5.23.



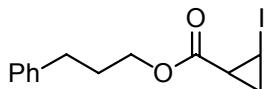
Methyl trans-10-(2-Iodocyclopropyl)decanoate: IR (neat): 2926, 2854, 1740, 1436, 1361, 1196, 1172, 1034 cm⁻¹; ¹HNMR (CDCl₃): δ 0.78 (ddd, J = 7.5, 6.0, 6.0 Hz, 1H), 0.89 (ddd, J = 9.0, 6.0, 4.2 Hz, 1H), 1.10-1.19 (m, 1H), 1.26-1.33 (m, 12H), 1.35-1.43 (m, 2H), 1.56-1.67 (m, 2H), 2.07 (ddd, J = 7.8, 3.9, 3.9 Hz, 1H), 2.30 (t, J = 7.5 Hz, 2H), 3.67 (s, 3H); ¹³CNMR (CDCl₃): δ -14.7, 16.5, 23.7, 24.9, 26.9, 28.6, 29.1, 29.1, 29.2, 29.3, 33.5, 34.1, 51.4, 174.3. Anal. Calcd for C₁₄H₂₅IO₂: C, 47.74; H, 7.15. Found: C, 47.97; H, 6.98.



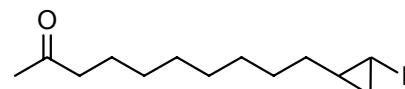
N,N-Dimethyl-[*trans*-10-(2-Iodocyclopropyl)]decanamide: IR (neat): 3542, 2924, 2853, 1649, 1463, 1397, 1265, 1145, 1034 cm⁻¹; ¹HNMR (CDCl₃): δ 0.78 (ddd, *J* = 7.5, 6.0, 6.0 Hz, 1H), 0.88 (ddd, *J* = 9.0, 6.0, 4.4 Hz, 1H), 1.10-1.19 (m, 1H), 1.23-1.42 (m, 14H), 1.59-1.66 (m, 2H), 2.07 (ddd, *J* = 7.8, 3.9, 3.9 Hz, 1H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.94 (s, 3H), 3.00 (s, 3H); ¹³CNMR (CDCl₃): δ -14.7, 16.5, 23.7, 25.1, 26.9, 28.7, 29.3, 29.4, 29.4, 33.4, 33.5, 35.3, 37.3, 173.2. Anal. Calcd for C₁₅H₂₈INO: C, 49.32; H, 7.73. Found: C, 49.08; H, 7.48.



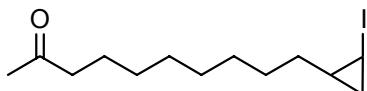
3-Phenylpropyl *trans*-2-Iodocyclopropanecarboxylate (*trans*-8): IR (neat): 3026, 2954, 1726, 1398, 1367, 1229, 1195, 1026 cm⁻¹; ¹HNMR (CDCl₃): δ 1.30 (ddd, *J* = 8.8, 5.8, 5.8 Hz, 1H), 1.62 (ddd, *J* = 8.2, 5.6, 5.6 Hz, 1H), 1.94-2.02 (m, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.75 (ddd, *J* = 8.3, 5.5, 3.6 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 7.18-7.40 (m, 5H); ¹³CNMR (CDCl₃): δ -17.1, 19.7, 24.6, 30.1, 32.1, 64.6, 126.1, 128.4, 128.5, 141.0, 172.0. Anal. Calcd for C₁₃H₂₃O₁: C, 47.29; H, 4.58. Found: C, 47.55; H, 4.57.



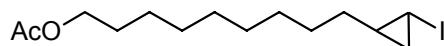
3-Phenylpropyl *cis*-2-Iodocyclopropanecarboxylate (*cis*-8): IR (neat): 3026, 2954, 2926, 1732, 1399, 1371, 1249, 1172 cm⁻¹; ¹HNMR (CDCl₃): δ 1.39-1.44 (m, 1H), 1.49-1.54 (m, 1H), 1.89 (ddd, *J* = 8.7, 7.4, 7.2 Hz, 1H), 1.97-2.06 (m, 2H), 2.73 (t, *J* = 7.8 Hz, 2H), 2.82 (ddd, *J* = 8.8, 7.3, 7.3 Hz, 1H), 4.15-4.27 (m, 2H), 7.18-7.31(m, 5H); ¹³CNMR (CDCl₃): δ -14.6, 16.4, 19.3, 30.4, 32.2, 64.6, 126.0, 128.4, 128.4, 141.2, 169.9. Anal. Calcd for C₁₃H₂₃O₁: C, 47.29; H, 4.58. Found: C, 47.51; H, 4.56.



trans-10-(2-Iodocyclopropyl)-2-decanone (*trans*-14): IR (neat): 2925, 2853, 1717, 1437, 1358, 1192, 1163 cm⁻¹; ¹HNMR (CDCl₃): δ 0.80 (ddd, *J* = 7.0, 6.9, 6.0 Hz, 1H), 0.91 (ddd, *J* = 9.0, 6.0, 4.2 Hz, 1H), 1.10-1.18 (m, 1H), 1.25-1.31 (m, 10H), 1.34-1.39 (m, 2H), 1.54-1.60 (m, 2H), 2.08 (ddd, *J* = 7.8, 3.9, 3.9 Hz, 1H), 2.13 (s, 3H), 2.43 (t, *J*=7.4 Hz, 2H); ¹³CNMR (CDCl₃): δ -14.7, 16.5, 23.7, 23.8, 28.7, 29.1, 29.2, 29.3, 29.9, 33.5, 43.8, 209.4. Anal. Calcd for C₁₃H₂₃O₁: C, 48.46; H, 7.19. Found: C, 48.74; H, 7.36.



cis-10-(2-Iodocyclopropyl)-2-decanone (cis-14): IR (neat): 2924, 2852, 1717, 1457, 1437, 1361, 1056 cm⁻¹; ¹HNMR (CDCl₃): δ 0.42-0.52 (m, 2H), 0.81-0.90 (m, 1H), 1.24-1.36 (m, 10H), 1.41-1.52 (m, 2H), 1.53-1.61 (m, 2H), 2.13 (s, 3H), 2.42 (t, J = 7.5 Hz, 2H), 2.58-2.65 (m, 1H); ¹³CNMR (CDCl₃): δ -6.1, 15.6, 15.8, 23.8, 28.5, 29.1, 29.3, 29.3, 29.4, 29.8, 35.0, 43.8, 209.4. Anal. Calcd for C₁₃H₂₃OI: C, 48.46; H, 7.19. Found: C, 48.56; H, 7.37.



trans-9-(2-Iodocyclopropyl)nonyl acetate (15): IR (neat): 2925, 2854, 1741, 1365, 1240, 1036 cm⁻¹; ¹HNMR (CDCl₃): δ 0.77 (ddd, J = 12.0, 7.5, 6.0 Hz, 1H), 0.89 (ddd, J = 9.1, 5.9, 4.4 Hz, 1H), 1.09-1.17 (m, 1H), 1.21-1.41 (m, 14H), 1.56-1.66 (m, 2H), 2.04 (s, 3H), 2.05-2.08 (m, 1H), 4.04 (t, J = 6.8 Hz, 2H); ¹³CNMR (CDCl₃): δ -14.7, 16.5, 21.0, 23.7, 25.9, 28.6, 28.7, 29.2, 29.3, 29.4, 29.4, 33.5, 64.6, 171.2. Anal. Calcd for C₁₄H₂₅IO₂: C, 47.74; H, 7.15. Found: C, 48.03; H, 6.93.

References

1. Charette, A. B., Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718-8719.