Supporting Information

Disulfidation of Alkynes and Alkenes with Gallium trichloride

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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. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzene was dried over slices of sodium. Gallium trichloride was purchased from Aldrich and was diluted in a glove box under argon to prepare 1.0 M hexane solution.

Experimental Section

A Typical Procedure for Disulfidation of Alkyne with GaCl_3 .

Gallium trichloride (0.50 mmol, 1.0 M hexane solution, 0.50 mL) was added to a benzene solution (2 mL) of diphenyl disulfide (**2a**, 0.50 mmol, 109 mg) and 1-octyne (**1a**, 0.75 mmol, 83 mg) at 0 °C under argon. The solution turned brown. After being stirred for 20 min, the mixture was poured into 1 M HCl solution, and the product was extracted with ethyl acetate (20 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 and was concentrated in vacuo. Purification of the residual oil

by silica gel column chromatography provided (*E*)-1,2-di(phenylthio)-1-octene (**3a**, 136 mg, *E/Z* > 20/1) in 83% yield.

A Typical Procedure for Disulfidation of Alkene with GaCl₃.

Gallium trichloride (0.50 mmol, 1.0 M hexane solution, 0.50 mL) was added to a benzene solution (2 mL) of diphenyl disulfide (**2a**, 0.50 mmol, 109 mg) and cyclopentene (**5a**, 1.0 mmol, 68 mg) at 0 °C under argon. The solution turned brown. After being stirred for 40 min, the mixture was poured into 1 M HCl solution, and the product was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over Na₂SO₄ and was concentrated in vacuo. Purification of the residual oil by silica gel column chromatography provided *trans*-1,2-di(phenylthio)-cyclopentane (**6a**, 125 mg) in 87% yield.

Characterization Data

Compounds **3a**¹, **3b**², **3c**², **3d**³, **3e**³, **3l**⁴, and **6a**⁵ were in the literature.

We assigned the stereochemistry of the known compounds such as **3a** and **6a** by the ¹H NMR spectrum previously reported. We decided the stereochemistry of the compounds by comparing their ¹H NMR spectra with those of analogous compound such as **3a** and **6a**.

(*E*)-1,2-Di(phenylthio)-1-(4-trifluoromethylphenyl)ethene (3f): IR (neat) 3061, 1614, 1583, 1479, 1441, 1406, 1323, 1128, 1067, 1016, 934, 847, 739, 689 cm⁻¹; ¹H NMR (CDCl₃) δ 7.06 (s, 1H), 7.12–7.42 (m, 10H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (CDCl₃) δ 125.04, 125.09, 126.88, 127.05, 127.43, 128.95, 129.21, 129.28, 129.76, 132.34, 134.49, 134.79, 140.77. HRMS Found: 388.0568. Calcd for C₂₁H₁₅F₃S₂: 388.0567.

(*E*)-1,2-Di(phenylthio)-1-(4-methoxyphenyl)ethene (3g): IR (neat) 3057, 2835, 1607, 1582, 1539, 1504, 1439, 1288, 1248, 1165, 1086, 1032, 941, 800, 689 cm⁻¹; ¹H NMR (CDCl₃) δ 3.76 (s, 3H), 6.82 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 2H), 7.22–7.32 (m, 1H), 7.55 (d, *J* = 7.5 Hz, 2H); ¹³C NMR

(CDCl₃) δ 55.19, 113.39, 126.50, 126.85, 127.72, 128.77, 129.00, 129.10, 129.25, 129.79, 130.36, 132.24, 135.19, 135.72, 159.22. HRMS Found: 350.0783. Calcd for C₂₁H₁₈OS₂: 350.0799.

(*E*)-1,2-Di(4-methylphenylthio)-1-octene (3i): IR (neat) 3020, 2955, 2926, 2856, 1597, 1491, 1454, 1211, 1180, 1090, 1016, 806 cm⁻¹; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.20–1.40 (m, 6H), 1.50–1.64 (m, 2H), 2.31 (s, 3H), 2.33 (s, 3H), 2.39 (t, *J* = 7.8 Hz, 3H), 6.20 (s, 1H), 7.06–7.22 (m, 6H), 7.30 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (CDCl₃) δ 14.19, 21.08, 21.22, 22.66, 28.25, 28.85, 31.66, 32.78, 122.83, 128.72, 129.66, 129.80, 129.95, 131.96, 132.51, 136.19, 137.42, 138.51. HRMS Found: 356.1638. Calcd for C₂₂H₂₈S₂: 356.1632.

(*E*)-1,2-Di(butylthio)-1-octene (3j): IR (neat) 2957, 2930, 2858, 1466, 1379, 1273, 1223, 1126, 808 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 6H), 1.20–1.36 (m, 6H), 1.38–1.66 (m, 10H), 2.32 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 5.84 (s, 1H); ¹³C NMR (CDCl₃) δ 13.77, 13.81, 14.21, 21.80, 22.11, 22.71, 28.17, 29.00, 31.07, 31.66, 31.74, 32.37, 33.39, 34.29, 120.44, 134.88. HRMS Found: 288.1951. Calcd for C₁₆H₃₂S₂: 288.1945.

(*E*)-1,2-Di(1-methylpropylthio)-1-octene (3k): IR (neat) 2961, 2928, 2856, 1560, 1460, 1377, 1294, 1221, 1150, 997, 808 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.24–1.34 (m, 6H), 1.42–1.72 (m, 6H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.76–3.02 (m, 2H), 6.12 (s, 1H); ¹³C NMR (CDCl₃) δ 11.50, 11.59, 14.21, 20.29, 21.23, 22.72, 28.02, 29.02, 29.43, 30.07, 31.76, 33.74, 41.89, 44.69, 123.72, 134.11. HRMS Found: 288.1953. Calcd for C₁₆H₃₂S₂: 288.1945.

(*E*)-1,2-Di(butylthio)-1-phenylethene (3m): IR (neat) 3055, 2957, 2928, 2872, 1597, 1545, 1487, 1464, 1443, 1379, 1273, 1225, 1099, 1030, 939, 804, 764, 696 cm⁻¹; ¹H NMR (CDCl₃) δ 0.83 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.20–1.52 (m, 6H), 1.52–1.68 (m, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 6.54 (s, 1H), 7.22–7.32 (m, 1H), 7.32–7.42 (m, 2H), 7.48–7.54 (m, 2H);

^{13}C NMR (CDCl_3) δ 13.60, 13.61, 21.63, 21.69, 31.31, 32.24, 32.54, 34.61, 127.70, 127.85, 128.15, 129.06, 130.67, 137.69. HRMS Found: 280.1326. Calcd for $\text{C}_{16}\text{H}_{24}\text{S}_2$: 280.1319.

***meso*-3,4-Di(phenylthio)hexane (6b):** IR (nujol) 1580, 1462, 1377, 1157, 1086, 1022, 872, 793, 746, 702, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.03 (t, $J = 7.2$ Hz, 6H), 1.62–1.78 (m, 2H), 1.80–1.96 (m, 2H), 3.20–3.28 (m, 2H), 7.16–7.30 (m, 6H), 7.34–7.40 (m, 4H); ^{13}C NMR (CDCl_3) δ 12.32, 25.79, 56.66, 126.53, 128.72, 131.61, 136.31. HRMS Found: 302.1149. Calcd for $\text{C}_{18}\text{H}_{22}\text{S}_2$: 302.1163.

***dl*-3,4-Di(phenylthio)hexane (6c):** IR (neat) 3057, 2964, 2930, 1583, 1481, 1439, 1377, 1304, 1092, 1024, 808, 739, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, $J = 7.2$ Hz, 6H), 1.22–1.42 (m, 2H), 2.06–2.18 (m, 2H), 3.06–3.14 (m, 2H), 7.08–7.22 (m, 10H); ^{13}C NMR (CDCl_3) δ 13.17, 22.00, 55.61, 126.54, 128.75, 131.54, 135.53. HRMS Found: 302.1158. Calcd for $\text{C}_{18}\text{H}_{22}\text{S}_2$: 302.1163.

1,2-Diphenylthiododecane (6d): IR (neat) 3059, 2926, 2855, 1583, 1479, 1439, 1377, 1089, 1069, 1026, 739, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.38 (m, 10H), 1.40–1.68 (m, 3H), 1.90–2.04 (m, 1H), 2.90 (dd, $J = 7.8, 13.2$ Hz, 1H), 3.04–3.14 (m, 1H), 3.24 (dd, $J = 3.0, 13.2$ Hz, 1H), 7.12–7.36 (m, 10H); ^{13}C NMR (CDCl_3) δ 14.12, 22.66, 26.73, 29.24, 29.35, 29.39, 31.85, 32.52, 39.34, 48.30, 126.21, 127.17, 128.89, 128.93, 129.73, 132.50, 134.34, 135.83. HRMS Found: 358.1803. Calcd for $\text{C}_{22}\text{H}_{30}\text{S}_2$: 358.1789.

***meso*-4,5-Di(phenylthio)octane (6e):** IR (neat) 1583, 1479, 1439, 1379, 1088, 1024, 741 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 7.2$ Hz, 6H), 1.20–1.86 (m, 8H), 3.28–3.36 (m, 2H), 7.10–7.28 (m, 6H), 7.32–7.48 (m, 4H); ^{13}C NMR (CDCl_3) δ 13.93, 20.88, 34.87, 54.85, 126.48, 128.70, 131.55, 136.36. HRMS Found: 330.1462. Calcd for $\text{C}_{20}\text{H}_{26}\text{S}_2$: 330.1476.

2-Ethyl-1,2-di(phenylthio)butane (6f): IR (neat) 3057, 2968, 2935, 1583, 1479, 1439, 1375, 1090, 1069, 1026, 914, 750, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 6H), 1.40–1.60 (m, 4H),

2.94 (s, 2H), 7.05–7.12 (m, 2H), 7.15–7.33 (m, 7H), 7.48–7.54 (m, 1H); ^{13}C NMR (CDCl_3) δ 8.34, 28.14, 42.19, 57.16, 125.77, 128.59, 128.75, 128.89, 129.33, 130.83, 137.31, 137.40. HRMS Found: 302.1156. Calcd for $\text{C}_{18}\text{H}_{22}\text{S}_2$: 302.1163.

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