Reversed Stereoselectivity in Iodohydroxylation of Allenyl Sulfides. An Efficient Synthesis of *Z*-3-Organosulfur-2-iodo-2-propenols

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Supporting Information

Experimental section

Typical procedure for the formation of **2:** A solution of allenyl phenyl sulfide(**1a**) (62 mg, 0.25 mmol) in 1 mL of CH₃CN was added slowly to a solution of iodine (127 mg, 0.5 mmol) in CH₃CN (7 mL) and water (2 mL) under a N₂ atmosphere. After being stirred at 15°C for about 16 hours, a saturated aqueous solution of Na₂S₂O₃ was added. The mixture was extracted with ether (25 mL x 3) and dried over MgSO₄. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) afforded **2a** (21 mg, 30%, *E/Z* = 1.08/1) as a solid.

***E*-2-Iodo-3-methyl-4-phenylbut-2-enal (*E*-**2a**).** solid; m.p. 65-67°C(*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ9.19 (s, 1 H), 7.22-7.27 (m, 3 H), 7.07-7.09 (m, 2 H), 4.10 (s, 2 H) 2.15 (s, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ184.65, 165.45, 136.34, 128.99, 128.46, 127.27, 109.54, 41.10, 32.43; IR (KBr) (cm⁻¹) = 3080, 3058, 3021, 2926, 2855, 1660, 1585, 1575, 1492, 1448, 1396, 1369, 1224, 1185, 1089, 1073, 1030; MS(70 eV, EI) *m/z*(%): 286(M⁺, 3.50), 91(100); HRMS Calcd for C₁₁H₁₁IO: 285.98546. Found:

285.98692.

Z-2-Iodo-3-methyl-4-phenylbut-2-enal (Z-2a). solid; m.p. 79-81°C(*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 9.17 (s, 1 H), 7.24-7.33 (m, 5 H), 3.99 (s, 2 H) 2.33 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 185.32, 165.22, 136.35, 128.85, 128.73, 127.23, 108.30, 52.41, 20.25; IR (KBr) (cm^{-1}) = 3022, 1681, 1664, 1585, 1493, 1450, 1430, 1246, 1091, 1071, 1029, 732; MS(70 eV, EI) $m/z(\%)$: 286(M^+ , 15.65), 91(100); HRMS Calcd for $\text{C}_{11}\text{H}_{11}\text{IO}$: 285.98546. Found: 285.98558.

Typical procedure for the formation of Z-4a: A solution of allenyl phenyl sulfide (64 mg, 0.25 mmol) in 1 mL of acetone was added slowly to a solution of iodine (127 mg, 0.5 mmol) in acetone (7 mL) and water (2 mL). After being stirred at r.t. for about 13 h, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added. The mixture was extracted with ether (25 mL x 3) and dried over MgSO_4 . Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) afforded **Z-4a** (68 mg, 68%) as an oil.

(1) Z-3-Iodo-2-methyl-1-phenyl-4-(phenylsulfanyl)but-3-en-2-ol (Z-4a).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.36 (m, 10 H), 6.80 (s, 1 H), 3.21 (d, J = 13.2 Hz, 1H), 2.96 (d, J = 13.8 Hz, 1 H), 2.11 (s, 1 H) 1.56 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 136.04, 134.12, 133.70, 130.61, 130.43, 129.11, 128.21, 127.46, 126.93, 111.26, 77.43, 47.17, 28.00; IR (KBr) (cm^{-1}) = 3538, 3449, 3059, 3027, 2927, 2925,

1581, 1568, 1478, 1452, 1440, 1372, 1341, 1239, 1113, 1090, 860, ; MS(70 eV, EI) m/z(%): 396(M⁺, 0.95), 43(100); HRMS Calcd for C₁₇H₁₇IOS: 396.00448. Found: 396.00417.

(2) Z-3-Iodo-4-(phenylsulfanyl)but-3-en-2-ol (Z-4b).

Oil; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.44 (m, 2 H), 7.25-7.35 (m, 3 H), 7.07 (s, 1 H), 4.03 (q, *J* = 6.0 Hz, 1 H), 2.71 (bs, 1 H), 1.32 (d, *J* = 6.0 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 133.55, 133.35, 130.77, 129.20, 127.67, 109.79, 73.95, 23.77; IR (KBr) (cm⁻¹) = 3373, 2976, 2926, 1579, 1479, 1439, 1369, 1126, 1069, 817; MS(70 eV, EI) m/z(%): 306(M⁺, 49.30), 69(100); HRMS Calcd for C₁₀H₁₁IOS: 305.95753. Found: 305.95662.

(3) Z-2-Iodo-4-methyl-1-(phenylsulfanyl)pent-1-en-3-ol (Z-4c).

Oil; ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.45 (m, 2 H), 7.28-7.37 (m, 3 H), 7.04 (s, 1 H), 3.28 (d, *J* = 8.1 Hz, 1 H), 1.82-1.93(m, 2 H), 1.05 (d, *J* = 6.1 Hz, 3 H), 0.84 (d, *J* = 6.9 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 134.63, 133.78, 130.82, 129.28, 127.72, 108.82, 83.47, 33.93, 19.16, 17.79; IR (KBr) (cm⁻¹) = 3402, 2961, 2929, 2871, 1581, 1478, 1468, 1440, 1385, 1070, 1025, 864, 809; MS (70 eV, EI) m/z(%): 334(M⁺, 19.82), 291(100); HRMS Calcd for C₁₂H₁₅IOS: 333.98883. Found: 333.99041.

(4) Z-2-Iodo-1-(phenylsulfanyl)hepta-1-en-3-ol (Z-4d).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.45 (m, 2 H), 7.29-7.37 (m, 3 H), 7.06 (s, 1 H), 3.72 (t, $J = 6.6$ Hz, 1 H), 2.08 (bs, 1 H), 1.62 (q, $J = 6.9$ Hz, 2 H), 1.22-1.39 (m, 4 H), 0.91 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.23, 133.72, 130.85, 129.27, 127.74, 109.47, 77.94, 36.86, 29.29, 22.37, 13.97; IR (KBr) (cm^{-1}) = 3375, 2955, 2928, 2857, 1580, 1479, 1465, 1440, 1025, 825; MS(70 eV, EI) $m/z(\%)$: 348(M^+ , 1.28), 41(100); HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{IOS}$: 348.00448. Found: 348.00211.

(5) Z-2-Iodo-1-(phenylsulfanyl)dec-1-en-3-ol (Z-4e).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.45 (m, 2 H), 7.26-7.37 (m, 3 H), 7.06 (d, $J = 0.6$ Hz, 1 H), 3.71 (t, $J = 6.6$ Hz, 1 H), 1.95 (bs, 1 H), 1.62 (q, $J = 6.6$ Hz, 2 H), 1.22-1.29 (m, 10 H), 0.88 (t, $J = 6.6$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.53, 134.04, 131.16, 129.57, 128.04, 109.81, 78.26, 37.46, 32.02, 29.53, 29.43, 25.46, 22.89, 14.37; IR (KBr) (cm^{-1}) = 3373, 2925, 2854, 1580, 1478, 1439, 1024, 823; MS(70 eV, EI) $m/z(\%)$: 390(M^+ , 24.33), 43(100); HRMS Calcd for $\text{C}_{16}\text{H}_{23}\text{IOS}$: 390.05143. Found: 390.05517.

(6) Z-3-Iodo-1-phenyl-4-(phenylsulfanyl)but-3-en-2-ol (Z-4f).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.36 (m, 10 H), 6.85 (s, 1 H), 4.03 (t, $J = 6.6$ Hz, 1 H), 3.00 (dd, $J' = 13.5$ Hz, $J'' = 6.3$ Hz, 1 H), 2.91 (dd, $J' = 13.5$ Hz, $J'' = 6.9$ Hz, 1 H), 2.15 (bs, 1 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 136.83, 134.72, 133.65, 130.67, 129.55, 129.16, 128.48, 127.60, 126.69, 107.71, 78.97, 43.35; IR (KBr) (cm^{-1}) = 3409, 3059, 3026, 2923, 2855, 1723, 1581, 1478, 1440, 1373, 1247, 1085, 1042, 826; MS(70 eV, EI) $m/z(\%)$: 382(M^+ , 5.59), 291(100); HRMS Calcd for $\text{C}_{16}\text{H}_{15}\text{IOS}$: 381.98883. Found: 381.98958.

(7) Z-3-Iodo-2-methyl-4-(phenylsulfanyl)but-3-en-2-ol (Z-4g).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.47 (m, 2 H), 7.31-7.34 (m, 3 H), 7.03 (s, 1 H), 2.10 (bs, 1 H), 1.51 (d, $J = 1.5$ Hz, 6 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.04, 132.44, 130.92, 129.27, 127.71, 113.59, 75.00, 29.68; IR (KBr) (cm^{-1}) = 3403, 2979, 2928, 1582, 1479, 1440, 1364, 1207, 1167, 1012, 925, 860; MS(70 eV, EI) $m/z(\%)$: 320(M^+ , 51.98), 305(100); HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{IOS}$: 319.97318. Found: 319.97310.

(8) Z-2-Iodo-3-methyl-1-(phenylsulfanyl)pent-1-en-3-ol (Z-4h).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.46 (m, 2 H), 7.27-7.36 (m, 3 H), 7.05 (s, 1 H),

2.10 (s, 1 H), 1.67-1.82 (m, 2 H), 1.49 (s, 3 H), 0.85 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.11, 132.92, 130.64, 129.17, 127.50, 111.91, 77.42, 34.53, 26.98, 8.06; IR (KBr) (cm^{-1}) = 3425, 2967, 2929, 2876, 1581, 1478, 1457, 1440, 1374, 1159, 1121, 1024, 947, 911, 860; MS(70 eV, EI) $m/z(\%)$: 334(M^+ , 19.13), 305(100); HRMS Calcd for $\text{C}_{12}\text{H}_{15}\text{IOS}$: 333.98883. Found: 333.98984.

(9) Z-2-Iodo-3,5-dimethyl-1-(phenylsulfanyl)hex-1-en-3-ol (Z-4i).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.39 (m, 2 H), 7.20-7.29 (m, 3 H), 7.01 (s, 1 H), 1.76 (s, 1 H), 1.60-1.71 (m, 2H), 1.49-1.54 (m, 1H), 1.43 (s, 3 H), 0.90 (d, $J = 3.3$ Hz, 3 H), 0.87 (d, $J = 3.3$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.24, 132.52, 130.68, 129.22, 127.53, 112.47, 77.87, 49.86, 28.87, 24.42, 24.34, 24.17; IR (KBr) (cm^{-1}) = 3447, 2953, 2927, 2868, 1528, 1568, 1478, 1466, 1440, 1366, 1158, 1088, 877, 855 ; MS(70 eV, EI) $m/z(\%)$: 362(M^+ , 14.43), 305(100); HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{IOS} - \text{CH}_3(\text{C}_{13}\text{H}_{16}\text{IOS})$: 347.99666. Found: 347.00060.

(10) Z-2-Iodo-3,4,4-trimethyl-1-(phenylsulfanyl)pent-1-en-3-ol (Z-4j).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.37 (m, 2 H), 7.19-7.27 (m, 3 H), 7.01 (s, 1 H), 1.79 (s, 1 H), 1.47 (s, 3 H), 0.98 (s, 9 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 135.92, 134.37, 130.54, 129.21, 127.44, 108.08, 79.54, 39.41, 26.57, 26.40; IR (KBr) (cm^{-1}) = 3478, 2957, 2872, 1582, 1558, 1479, 1440, 1371, 1073, 901, 861; MS(70 eV, EI) $m/z(\%)$:

362(M^+ , 1.02), 305(100); HRMS Calcd for $C_{14}H_{19}IOS$: 362.02013. Found: 362.01818.

(11) Z-3-Ethyl-2-iodo-1-(phenylsulfanyl)pent-1-en-3-ol (Z-4k).

Oil; 1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.46 (m, 2 H), 7.27-7.37 (m, 3 H), 7.08 (s, 1 H), 1.83-1.93 (m, 2 H), 1.79 (s, 1H), 1.61-1.71 (m, 2 H), 0.87 (t, $J = 7.5$ Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 134.37, 133.47, 130.49, 129.17, 127.38, 109.31, 79.92, 32.59, 7.42; IR (KBr) (cm^{-1}) = 3470, 2967, 2933, 2877, 2852, 1581, 1478, 1458, 1440, 1376, 1158, 1088, 1024, 961, 865; MS(70 eV, EI) m/z (%): 348(M^+ , 20.01), 319(100); HRMS Calcd for $C_{13}H_{17}IOS$: 348.00448. Found: 348.00385.

(12) Z-2-Iodo-1-(phenylsulfanyl)-3-butylhepta-1-en-3-ol (Z-4l).

Oil; 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.38 (m, 2 H), 7.19-7.29 (m, 3 H), 6.99 (s, 1 H), 1.73-1.83 (m, 2 H), 1.68 (s, 1H), 1.52-1.58 (m, 2 H), 1.14-1.29 (m, 8 H), 0.84 (t, $J = 6.6$ Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 134.47, 132.89, 130.47, 129.17, 127.36, 110.05, 79.59, 40.06, 25.13, 22.82, 14.02; IR (KBr) (cm^{-1}) = 3475, 2955, 2870, 1723, 1582, 1570, 1478, 1465, 1440, 1380, 1252, 1089, 865; MS(70 eV, EI) m/z (%): 404(M^+ , 4.96), 347(100); HRMS Calcd for $C_{17}H_{25}IOS$: 404.06708. Found: 404.06309.

(13) Z-2-Iodo-1-(phenylsulfanyl)-5-pentyllocta-1-en-3-ol (Z-4m).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.39 (m, 2 H), 7.19-7.30 (m, 3 H), 6.99 (s, 1 H), 1.75-1.80 (m, 2 H), 1.66 (s, 1 H), 1.49-1.55 (m, 2 H), 1.18-1.28 (m, 12 H), 0.83 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 134.46, 132.81, 130.44, 129.15, 127.33, 110.19, 79.62, 40.26, 31.92, 22.64, 22.49, 14.04; IR (KBr) (cm^{-1}) = 3473, 2928, 2859, 1673, 1581, 1478, 1466, 1440, 1378, 1025, 872; MS(70 eV, EI) m/z (%): 432(M^+ , 5.36), 361(100); HRMS Calcd for $\text{C}_{19}\text{H}_{29}\text{IOS}$: 432.09838 Found :432.09890.

(14) Z-1-(1'-cyclohexenyl)-1-iodo-2-(phenylsulfanyl)ethene (Z-6n).

Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.50 (m, 2 H), 7.30-7.39 (m, 3 H), 6.91 (s, 1 H), 6.12 (t, $J = 3.9$ Hz, 1 H), 2.31-2.35 (m, 2 H), 2.17-2.22 (m, 2H), 1.57-1.70 (m, 4 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 135.81, 134.59, 132.32, 131.51, 130.52, 129.20, 127.45, 105.94, 27.13, 26.15, 22.79, 22.12; MS(70 eV, EI) m/z (%): 342(M^+ , 59.10), 218(100); HRMS Calcd for $\text{C}_{14}\text{H}_{15}\text{IS}$: 341.99392. Found: 341.99254.

1-(phenylsulfinyl)-2-iodohept-1-en-3-ol (Z-5a).

Oil, ^1H NMR (300 MHz, CDCl_3) less polar isomer: δ 7.70-7.73 (m, 2 H), 7.49-7.53 (m, 3

H), 7.11 (d, $J = 0.9$ Hz, 1 H), 4.12-4.15 (m, 1 H), 3.51 (bs, 1 H), 1.73-1.78 (m, 1 H), 1.47-1.54 (m, 1 H), 1.22-1.30 (m, 4 H), 0.81-0.88 (m, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.24, 140.79, 131.33, 129.45, 124.31, 124.28, 78.13, 35.00, 26.89, 22.33, 13.90; more polar isomer: δ 7.22-7.76 (m, 2 H), 7.50-7.52 (m, 3 H), 7.00 (s, 1 H), 3.79 (t, $J = 12.6$ Hz, 1 H), 2.80 (bs, 1 H), 1.55-1.64 (m, 2 H), 1.08-1.27 (m, 4 H), 0.81 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CD_3COCD_3) δ 145.40, 142.60, 137.32, 131.38, 129.71, 124.28, 77.07, 35.82, 27.15, 22.35, 13.61; IR (KBr) (cm^{-1}) = 3356, 2955, 2930, 2858, 1582, 1443, 1081, 1030, 997; MS(70 eV, EI) $m/z(\%)$: 364(M^+ , 5.84), 77(100); HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{IO}_2\text{S}$: 363.99940. Found: 364.00432.