Stereoselective Synthesis of (*Z*)-Enethiols and Their Derivatives: Vinylic S_N2 Reaction of (*E*)-Alkenyl(phenyl)-λ^3-iodanes with Thioamides

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Synthesis of (*Z*)-Enethiol 2: Reaction of (*E*)-(1-Decenyl)phenyliodonium Tetrafluoroborate (1a) with *N*,*N*-Dimethylthioformamide (Table 1, entry 1). To a stirred solution of (*E*)-(1-decenyl)phenyliodonium tetrafluoroborate (**1a**) (36 mg, 0.084 mmol) in dichloromethane (1.7 mL) was added *N*,*N*-dimethylthioformamide (22 mg, 0.25 mmol) at room temperature under nitrogen, and the mixture was stirred for 20 h. Water was added, the mixture was extracted with dichloromethane, and the combined organic phase was washed with water. The organic phase was filtered and concentrated under aspirator vacuum to give a pale yellow oil. Yields of the products (*Z*)-1-decene-1-thiol (**2a**, 70%) and iodobenzene (44%) were determined by ^{1}H NMR. Attempted removal of by-product iodobenzene under high vacuum resulted in dimerization of **2a** to give (*Z*)-1-decenyl 1-mercaptodecyl sulfide (**3a**).

(*Z*)-Enethiol 2a: colorless oil; IR ($CHCl_3$) 2250, 908 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.98 (ddt, *J* = 9.6, 8.6, 1.4 Hz, 1H), 5.66 (dt, *J* = 9.6, 7.1 Hz, 1H), 2.66 (d, *J* = 8.6 Hz, 1H), 2.10 (dq, *J* = 1.4, 7.1 Hz, 2H), 1.45-1.20 (m, 12H), 0.91 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 131.4 (d), 114.1 (d), 31.9 (t), 29.4 (t), 29.2 (t), 28.2 (t), 28.2 (t), 22.6 (t), 14.1 (q); MS *m/z* (relative intensity) 172 (26, M^+), 101 (14), 87 (28), 73 (64), 60 (100); HRMS calcd for $C_{10}H_{20}S$ (M^+) 172.1286, found 172.1297.

(*Z*)-Enethiol 2b: colorless oil; IR ($CHCl_3$) 2252, 1268, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33-7.14 (m, 5H), 6.03 (br t, *J* = 8.9 Hz, 1H), 5.69 (dt, *J* = 8.9, 7.0 Hz, 1H), 2.67 (d, *J* = 8.9 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.16 (br q, *J* = 7.0 Hz, 2H), 1.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 142.2 (s), 130.7 (d), 128.5 (d), 128.3 (d), 125.8 (d), 114.9 (d), 35.4 (t), 30.4 (t), 22.7 (t); MS *m/z* (relative intensity) 178 (5, M^+), 144 (32), 129 (21), 117 (26), 105 (36), 91 (100), 73 (26), 65 (38), 45 (57); HRMS calcd for $C_{11}H_{14}S$ (M^+) 178.0816, found 178.0814.

Dimer 3a: colorless oil; ^{1}H NMR ($CDCl_3$) δ 6.11 (dt, *J* = 9.6, 1.5 Hz, 1H), 5.73 (dt, *J* = 9.6, 7.3 Hz, 1H), 4.04 (q, *J* = 6.9 Hz, 1H), 2.19-2.08 (3H), 1.98-1.76 (m, 2H), 1.41-1.20 (m, 26H), 0.89 (t, *J* = 6.3 Hz, 6H).

The structure of **2a**, **2b**, and **3a** was determined by spectroscopy using two-dimensional (2D) NMR techniques, i.e., ^{1}H,^{1}H-COSY and ^{13}C,^{1}H-COSY.

(*Z*)-*S*-Vinylthioimidonium Salt 6a (R' = Me, R" = H, X = S): Reaction of 1a with Thioacetamide. To a stirred solution of **1a** (39 mg, 0.09 mmol) in dichloromethane (1.8 mL) was added thioacetamide (7.5 mg, 0.10 mmol) at room temperature under nitrogen, and the mixture was stirred for 24 h. The reaction mixture was concentrated under aspirator vacuum to give a pale yellow oil, which was washed several times with hexane by decantation to give (*Z*)-*S*-vinylthioimidonium salt **6a** (87% ^{1}H NMR yield) contaminated with a small amount of impurity.

(*Z*)-*S*-Vinylthioimidonium Salt 6a (R' = Me, R" = H, X = S): pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 9.6 (br s, 2H), 6.77 (dt, *J* = 8.7, 7.5 Hz, 1H), 6.21 (br d, *J* = 8.7 Hz, 1H), 2.68 (s, 3H), 2.29 (br q, *J* = 7.5 Hz, 2H), 1.51-1.22 (m, 12H), 0.88 (t, *J* = 6.3 Hz, 3H); FAB MS *m/z* 214 [(M-BF_4)$^+$]; HRMS (FAB) calcd for $C_{12}H_{24}NS$ [(M-BF_4)$^+$] 214.1629, found 214.1629.

(*Z*)-*S*-Vinylthioimidonium Salt 6b (R' = Ph, R" = H, X = S): pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.97 (br d, *J* = 7.4 Hz, 2H), 7.78 (br t, *J* = 7.3 Hz, 1H), 7.61 (br t, *J* = 7.4 Hz, 2H), 6.89 (dt, *J* = 8.7, 7.5 Hz, 1H), 6.42 (dt, *J* = 8.7, 1.2 Hz, 1H), 2.37 (br q, *J* = 7.5 Hz, 2H), 1.57-1.20 (m, 12H), 0.88 (t, *J* = 6.5 Hz, 3H); FAB MS *m/z* 276 [(M-BF_4)$^+$]; HRMS (FAB) calcd for $C_{17}H_{26}NS$ [(M-BF_4)$^+$] 276.1786, found 276.1794.

Synthesis of (*Z*)-*S*-Vinylisothiouronium Salt 10: Reaction of (*E*)-(1-Decenyl)phenyliodonium Tetrafluoroborate (1a) with Thiourea (9a) (Table 2, entry 1). A suspension of (*E*)-(1-decenyl)phenyliodonium tetrafluoroborate (**1a**) (76 mg, 0.18 mmol) and thiourea (**1a**) (15 mg, 0.20 mmol) in dichloromethane (3.6 mL) was stirred for 17 h at room temperature under nitrogen. Water was added, the mixture was extracted with dichloromethane, and the combined organic phase was washed with water. The organic phase was filtered and concentrated under aspirator vacuum to give a yellow oil, which was washed several times with hexane by decantation at -78 °C to give (*Z*)-*S*-vinylisothiouronium salt **10a** (41.5 mg, 77%).

(*Z*)-*S*-Vinylisothiouronium Salt 10a: colorless oil; IR (neat) 3430-3000, 1652, 1445, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28 (br s, NH), 6.68 (dt, *J* = 8.6, 7.5 Hz, 1H), 6.13 (dt, *J* = 8.6, 1.0 Hz, 1H), 2.33 (br q, *J* = 7.5 Hz, 2H), 1.44 (m, 2H), 1.35-1.24 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H); FAB MS *m/z* 215 [(M-BF_4)$^+$]; HRMS (FAB) calcd for $C_{11}H_{23}N_2S$ [(M-BF_4)$^+$] 215.1582, found 215.1574.

(*Z*)-*S*-Vinylisothiouronium Salt 10b: colorless oil; IR (neat) 3360, 1655, 1611, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.72 (dt, *J* = 8.7, 7.6 Hz, 1H), 6.11 (dt, *J* = 8.7, 1.1 Hz, 1H), 3.09 (s, 3H), 2.33 (br q, *J* = 7.6 Hz, 2H), 1.53-1.20 (m, 12H) 0.90 (t, *J* = 6.5 Hz, 3H); FAB MS *m/z* 229 [(M-BF_4)$^+$], HRMS (FAB) calcd for $C_{12}H_{25}N_2S$ [(M-BF_4)$^+$] 229.1738, found 229.1729.

(*Z*)-*S*-Vinylisothiouronium Salt 10c: pale yellow oil; IR (neat) 3330, 1635, 1529, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30 (br s, NH), 6.77 (dt, *J* = 8.8, 7.4 Hz, 1H), 6.09 (dt, *J* = 8.8, 1.1 Hz, 1H), 3.15 (br s, 3H), 3.09 (br s, 3H), 2.33 (br q, *J* = 7.4 Hz, 2H), 1.52-1.23 (m, 12H), 0.88 (t, *J* = 6.3 Hz, 3H); FAB MS *m/z* 243 [(M-BF_4)$^+$]; HRMS (FAB) calcd for $C_{13}H_{27}N_2S$ [(M-BF_4)$^+$] 243.1895, found 243.1886.

(*Z*)-*S*-Vinylisothiouronium Salt 10d: colorless oil; IR (neat) 1608, 1508, 1467, 1403, 1062 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.18 (dt, *J* = 8.9, 8.4 Hz, 1H), 6.07 (dt, *J* = 8.9, 1.0 Hz, 1H), 3.34 (s, 12H), 2.21 (br q, *J* = 8.4 Hz, 2H), 1.50-1.23 (m, 12H), 0.88 (t, *J* = 6.5 Hz, 3H); FAB MS *m/z* 271 $[(M\text{-}BF_4)^+]$, HRMS (FAB) calcd for $C_{15}H_{31}N_2S$ $[(M\text{-}BF_4)^+]$ 271.2208, found 271.2196.

(*Z*)-*S*-Vinylisothiouronium Salt 10e: yellow oil; IR (neat) 3326, 1645, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50-7.28 (m, 5H), 6.68 (dt, *J* = 8.8, 8.0 Hz, 1H), 6.24 (br s, NH), 6.14 (dt, *J* = 8.8, 1.1 Hz, 1H), 2.29 (br q, *J* = 8.0 Hz, 2H), 1.49-1.21 (m, 12H), 0.88 (t, *J* = 6.2 Hz, 3H); FAB MS *m/z* 291 $[(M\text{-}BF_4)^+]$; HRMS (FAB) calcd for $C_{17}H_{27}N_2S$ $[(M\text{-}BF_4)^+]$ 291.1895, found 291.1883.

(*Z*)-*S*-Vinylisothiouronium Salt 10f: colorless plates; mp 29-31 °C (recrystallized from CH_2Cl_2-Et_2O-hexane); IR (KBr) 3375, 1563, 1058 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03 (br s, NH), 6.55 (dt, *J* = 8.6, 7.4 Hz, 1H), 6.18 (dt, *J* = 8.6, 1.0 Hz, 1H), 4.03 (s, 4H), 2.29 (br q, *J* = 7.4 Hz, 2H), 1.50-1.20 (m, 12H), 0.89 (t, *J* = 6.5 Hz, 3H); FAB MS *m/z* 241 $[(M\text{-}BF_4)^+]$; HRMS (FAB) calcd for $C_{13}H_{25}N_2S$ $[(M\text{-}BF_4)^+]$ 241.1738, found 241.1734.

(*Z*)-*S*-Vinylisothiourea 11c: colorless oil; IR (neat) 3250, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.17 (dt, *J* = 9.7, 1.1 Hz, 1H), 6.07 (dt, *J* = 9.7, 6.9 Hz, 1H), 4.16 (br s, 1H, NH), 2.98 (br s, 6H), 2.25 (br q, *J* = 6.9 Hz, 2H), 1.45-1.23 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H); MS *m/z* (relative intensity) 242 (60, M^+), 212 (20), 172 (25), 129 (63), 95 (40), 81 (57), 70 (95), 56 (100); HRMS calcd for $C_{13}H_{26}N_2S$ (M^+) 242.1817, found 242.1807.

(*Z*)-*S*-Vinylisothiourea 11g: pale yellow powder; mp 80.5-83.5 °C (recrystallized from CH_2Cl_2-hexane); IR (KBr) 3430, 1729, 1474, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.25 (br s, 1H, NH), 6.53 (br d, *J* = 9.1 Hz, 1H), 6.05 (dt, *J* = 9.1, 7.5 Hz, 1H), 4.20 (s, 2H), 2.20 (br q, *J* = 7.5 Hz, 2H), 1.49-1.23 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H); MS *m/z* (relative intensity) 254 (15, M^+), 221 (19), 197 (13), 169 (45), 155 (25), 141 (100), 117 (18), 85 (18), 68 (18), 55 (46). Anal. Calcd for $C_{13}H_{22}N_2OS$: C, 61.38; H, 8.72; N, 11.01. Found: C, 60.91; H, 8.54; N, 10.93.

Synthesis of (*Z*)-Vinyl Sulfides 15: Reaction of (*E*)-(1-Decenyl)phenyliodonium Tetrafluoroborate (1a) with 2-Mercaptobenzimidazole (13a) (Table 3, entry 1). A solution of (*E*)-(1-decenyl)phenyliodonium tetrafluoroborate (**1a**) (44 mg, 0.10 mmol) and 2-mercaptobenzimidazole (**13a**) (19 mg, 0.12 mmol) in dichloromethane (2.1 mL) was stirred for 9 h at room temperature under nitrogen. Water was added, the mixture was extracted with dichloromethane, and the combined organic phase was washed with water. The organic phase was filtered and concentrated under aspirator vacuum to give a pale yellow solid, which was purified by preparative TLC to give (*Z*)-vinyl sulfide **15a** (24 mg, 80%).

(*Z*)-Vinyl Sulfide 15a: colorless needles; mp 114-115.5 °C (recrystallized from CH_2Cl_2-hexane); IR (KBr) 1634, 1441, 1407, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58-7.50 (m, 2H), 7.24-7.16 (m, 2H), 6.64 (dt, *J* = 9.1, 1.0 Hz, 1H), 5.95 (dt, *J* = 9.1, 7.4 Hz, 1H), 2.21 (br q, *J* = 7.4 Hz, 2H), 1.47-1.20 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 3H); MS *m/z* (relative intensity) 288 (34, M^+), 255 (75), 175 (100). Anal. Calcd for $C_{17}H_{24}N_2S$: C, 70.79; H, 8.39; N, 9.71. Found: C, 70.38; H, 8.28; N,

9.55.

(*Z*)-Vinyl Sulfide 15b: colorless oil; IR (neat) 1605, 1505, 1454, 1133 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.66-7.59 (m, 1H), 7.48-7.42 (m, 1H), 7.32-7.23 (m, 2H), 6.70 (dt, *J* = 9.1, 1.2 Hz, 1H), 6.06 (dt, *J* = 9.1, 7.4 Hz, 1H), 2.26 (br q, *J* = 7.4 Hz, 2H), 1.55-1.20 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H); MS *m/z* 289 (M^+), 256, 232, 204, 176, 151, 133, 120, 55; HRMS calcd for $C_{17}H_{23}NOS$ (M^+) 289.1500, found 289.1499.

(*Z*)-Vinyl Sulfide 15c: colorless oil; IR (neat) 1610, 1427, 997, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (br d, *J* = 8.4 Hz, 1H), 7.77 (br d, *J* = 8.3 Hz, 1H), 7.48-7.24 (m, 2H), 6.67 (dt, *J* = 8.9, 1.2 Hz, 1H), 6.10 (dt, *J* = 8.9, 7.5 Hz, 1H), 2.29 (br q, *J* = 7.5 Hz, 2H), 1.53-1.15 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 3H); MS *m/z* 305 (M^+), 272, 248, 192, 167, 149; HRMS calcd for $C_{17}H_{23}NS_2$ (M^+) 305.1272, found 305.1279.

(*Z*)-Vinyl Sulfide 15d: colorless oil; IR (neat) 1605, 1457, 1427, 997, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (br d, *J* = 8.0 Hz, 1H), 7.77 (br d, *J* = 8.0 Hz, 1H), 7.43 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.35-7.13 (m, 6H), 6.72 (dt, *J* = 9.0, 1.2 Hz, 1H), 6.11 (dt, *J* = 9.0, 7.3 Hz, 1H), 2.77 (t, *J*= 7.4 Hz, 2H), 2.34 (br q, *J* = 7.3 Hz, 2H), 1.80 (m, 2H); MS *m/z* (relative intensity) 311 (60, M^+), 278 (19), 220 (38), 192 (100), 91; HRMS calcd for $C_{18}H_{17}NS_2$ (M^+) 311.0802, found 311.0801.