Structure-dependent oxidative bromination of unsaturated C-C

bonds mediated by Selectfluor

Chengfeng Ye and Jean'ne M. Shreeve*

*Department of Chemistry, University of Idaho, Moscow, Idaho
83844-2343*

E-mail: jshreeve@uidaho.edu

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Experimental Section

General. All the reagents used were analytical reagents purchased from commercial sources and used as received. ^1H , ^{19}F , and ^{13}C NMR spectra were recorded on a spectrometer operating at 300, 282, and 75 MHz, respectively, in CDCl_3 unless otherwise stated. Chemical shifts are reported in ppm relative to the appropriate standard, CFCl_3 for ^{19}F and TMS for ^1H and ^{13}C NMR spectra.

General procedure: To a stirred mixture of olefin (10 mmol) and KBr (35 mmol), CH_3CN (25 mL), methanol or water (1 mL) and Selectfluor (13 mmol) was added. The reaction was monitored by TLC. After completion of the reaction, it was diluted with water and extracted with CH_2Cl_2 (25 mL x 3). The organic layers were combined and washed with dilute solutions of NaHCO_3 , Na_2SO_3 and brine. It was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude products, which were purified by column chromatography packed with silica gel to afford the pure products.

1-(1-bromo-2-methoxypropan-2-yl)benzene (3a)¹

^1H NMR δ 3.33 (s, 1H), 3.49 (dd, 1H, $J = 10.6, 4.4$ Hz), 3.57 (dd, 1H, $J = 10.6, 8.1$ Hz), 4.42 (dd, 1H, $J = 8.1, 4.4$ Hz), 7.33-7.43 (m, 5H), ^{13}C NMR δ 37.2, 58.1, 84.3, 127.7, 129.4, 129.6, 140.0.

1-(2-bromo-1-methoxyethyl)benzene (3b)¹

^1H NMR δ 1.75 (s, 3H), 3.18 (s, 1H), 3.55 (d, 1H, $J = 10.6$ Hz), 3.67 (d, 1H, $J = 10.6$ Hz), 7.33-7.46 (m, 5H), ^{13}C NMR δ 22.8, 43.9, 51.9, 127.3, 128.7, 129.3, 142.7.

(±)-*trans*-1-bromo-2-methoxy-1,2-diphenylethane(3c)¹

¹H NMR δ 3.16 (s, 1H), 4.67 (d, 1H, *J* = 7.2 Hz), 5.06 (d, 1H, *J* = 7.2 Hz), 7.26-7.48 (m, 10H), ¹³C NMR δ 57.1, 58.1, 86.9, 129.3, 129.4, 129.5, 129.9, 130.0, 140.7, 142.0.

2-bromo-1-phenylethanol (3d)¹

¹H NMR δ 3.51 (s, 1H), 3.54 (dd, 1H, *J* = 10.4, 8.2 Hz), 3.60 (dd, 1H, *J* = 10.4, 4.0 Hz), 4.89 (dd, 1H, *J* = 8.2, 4.0 Hz), 7.34-7.42 (m, 5H), ¹³C NMR δ 40.6, 74.7, 127.1, 129.3, 129.6, 141.6.

1-(1,2-dibromoethyl)benzene (4d)¹

¹H NMR δ 4.07 (t, 1H, *J* = 10.2 Hz), 4.13 (dd, 1H, *J* = 10.2, 5.6 Hz), 5.20 (dd, 1H, *J* = 10.2, 5.6 Hz), 7.38-7.47 (m, 5H), ¹³C NMR δ 36.0, 51.9, 128.6, 129.8, 130.1, 139.6.

1-bromo-2-phenylpropan-2-ol (3e)¹

¹H NMR δ 1.74 (s, 3H), 3.75 (d, 1H, *J* = 10.4 Hz), 3.80 (d, 1H, *J* = 10.4 Hz), 7.35-7.64 (m, 5H), ¹³C NMR δ 29.0, 47.2, 74.1, 127.5, 128.5, 129.4, 145.2.

1-(1,2-dibromopropan-2-yl)benzene (4e)¹

¹H NMR δ 2.40 (s, 3H), 4.21 (d, 1H, *J* = 10.0 Hz), 4.44 (d, 1H, *J* = 10.0 Hz), 7.37-7.65 (m, 5H), ¹³C NMR δ 30.9, 41.2, 44.5, 127.5, 129.4, 129.5, 142.9.

(±)-trans-2-bromo-1,2-diphenylethanol (3f) ²

¹H NMR δ 5.13 (d, 1H, *J* = 6.6 Hz), 5.21 (d, 1H, *J* = 6.6 Hz), 7.22-7.42 (m, 10H), ¹³C NMR δ 59.9, 78.9, 128.0, 129.2, 129.3, 129.4, 129.7, 129.9, 138.6, 140.7.

meso-1,2-dibromo-1,2-diphenylethane (4f) ³

¹H NMR δ 5.50 (s, 2H), 7.28-7.47 (m, 6H), 7.53-7.56 (m, 4H), ¹³C NMR (CD₃CN) δ 55.1, 126.9, 127.8, 128.0, 139.1.

2-(bromomethyl)-5-(4-chlorophenyl)-tetrahydrofuran (5) ⁴

¹H NMR δ 1.89-1.97 (m, 2H), 2.14-2.26 (m, 2H), 3.47-3.35 (m, 2H), 4.26-4.30 (m, 0.37 H), 4.43-4.48 (m, 0.62 H), 4.93-4.96 (m, 0.37 H), 5.05-5.09 (m, 0.63 H), 7.25-7.38 (m, 4H), ¹³C NMR δ 31.2 (31.9), 35.2 (36.1), 36.7(36.8), 79.4 (79.6), 81.7(82.2), 127.8(128.0), 129.4, 135.9, 141.9 (142.1).

2-(bromomethyl)-octahydrobenzofuran (6) ⁵

¹H NMR δ 1.11-1.41 (m, 5H), 1.65-2.19(m, 6H), 3.19-3.34 (m, 1H), 3.36-3.49 (m, 2H), 4.20-4.27 (m, 1H). ¹³C NMR δ 25.04(25.07), 26.4 (26.6), 29.7 (29.8), 32.0 (32.1), 36.1 (37.2), 37.6 (37.9), 44.8 (47.1), 77.5 (78.2), 84.1 (85.4).

2,2-dibromo-1-phenylethanone (7) ⁶

¹H NMR δ 6.77 (s, 1H), 7.48-7.53 (m, 2H), 7.62-7.67 (m, 1H), 8.06-8.10 (m, 2H). ¹³C NMR δ 40.8, 129.9, 130.6, 131.7, 135.4, 187.2.

(*E*)-1-(1,2-dibromovinyl)benzene (8) ⁷

¹H NMR δ 6.84 (s, 1H), 7.41-7.57 (m, 5H), ¹³C NMR δ 103.9, 129.2, 130.0, 130.3, 132.9, 137.9.

3-bromobut-3-en-2-one (10) ⁸

¹H NMR δ 2.37 (s, 1H), 6.35 (d, 1H, *J* = 2.4 Hz), 6.73 (d, 1H, *J* = 2.4 Hz); ¹³C NMR δ 26.5, 130.4, 132.6, 192.4.

methyl 2-bromoacrylate (11) ⁸

¹H NMR δ 3.76 (s, 1H), 6.21 (d, 1H, *J* = 1.7 Hz), 6.73 (d, 1H, *J* = 1.7 Hz); ¹³C NMR δ 54.3, 121.8, 131.6, 163.1.

2-bromocyclohex-2-enone (12) ⁸

¹H NMR δ 2.08 (m, 2H), 2.45 (m, 2H), 2.63 (t, *J* = 7.2 Hz), 7.43 (t, 1H, *J* = 4.4 Hz); ¹³C NMR δ 23.5, 29.2, 39.2, 124.7, 152.1, 192.1.

2-bromocyclopent-2-enone (13) ⁸

¹H NMR δ 2.37 (m, 2H), 2.60 (m, 2H), 7.69 (t, 1H, *J* = 2.9 Hz); ¹³C NMR δ 28.9, 33.2, 126.7, 163.1, 202.5.

***erythro*-3,4-dibromo-4-phenylbutan-2-one (14)** ^{7a}

^1H NMR δ 2.50 (s, 3H), 4.96 (d, 1H, $J = 11.6$ Hz), 5.35 (d, 1H, $J = 11.6$ Hz), 7.35-7.45 (m, 5H); ^{13}C NMR δ 27.8, 50.4, 53.7, 129.0, 129.8, 130.2, 138.7, 199.2.

***erythro*-methyl 2,3-dibromo-3-phenylpropanoate (15)** ^{1a}

^1H NMR δ 3.92 (s, 3H), 4.88 (d, 1H, $J = 11.7$ Hz), 5.37 (d, 1H, $J = 11.7$ Hz), 7.39-7.44 (m, 5H); ^{13}C NMR δ 47.6, 51.5, 54.3, 128.9, 129.8, 130.3, 138.5, 169.2.

***erythro*-2,3-dibromo-1,3-diphenylpropan-1-one (16)** ³

^1H NMR δ 5.69 (d, 1H, $J = 11.3$ Hz), 5.88 (d, 1H, $J = 11.3$ Hz), 7.40-7.76 (m, 8H), 8.13-8.16 (m, 2H); ^{13}C NMR δ 47.7, 50.7, 129.3, 129.77, 129.8, 129.9, 130.2, 135.1, 135.3, 139.1, 192.1.

(*E*)-ethyl 2,3-dibromo-3-phenylacrylate (17) ⁹

^1H NMR δ 1.42 (t, 3H, $J = 7.1$ Hz), 4.40 (q, 2H, $J = 7.1$ Hz), 7.39-7.47 (m, 5H); ^{13}C NMR δ 14.9, 63.7, 108.6, 122.4, 129.3, 129.6, 130.6, 139.0, 164.8.

(*E*)-1,4-dimethoxy-1,4-diphenylbut-2-ene (21) ¹⁰

Two isomers. ^1H NMR δ 3.31 (s, 4.5 H), 3.36 (s, 1.5 H), 4.68-4.69 (m, 2H), 5.86-5.88 (m, 2H), 7.33-7.39 (m, 5H); ^{13}C NMR δ 57.28 (57.31), 84.47 (84.52), 127.7, 128.6, 129.35 (129.36), 133.5 (133.8), 141.8.

(*E*)-1-(2-bromovinyl)benzene (23) ¹¹

^1H NMR δ 6.79 (d, 1H, $J = 14.0$ Hz), 7.14 (d, 1H, $J = 14.0$ Hz), 7.31-7.36 (m, 5H); ^{13}C
NMR δ 107.4, 127.0, 129.1, 129.7, 136.8, 138.1.

(*E*)-1-(2-bromovinyl)-3-chlorobenzene (24)¹²

^1H NMR δ 6.83 (d, 1H, $J = 14.0$ Hz), 7.05 (d, 1H, $J = 14.0$ Hz), 7.26-7.71 (m, 4H); ^{13}C
NMR δ 109.1, 125.2, 129.2, 130.9, 137.5, 138.4.

(*E*)-4-(2-bromovinyl)phenol (25)¹³

^1H NMR δ 6.62 (d, 1H, $J = 14.0$ Hz), 6.81 (d, 1H, $J = 8.6$ Hz), 7.05 (d, 1H, $J = 14.0$ Hz),
7.20 (d, 1H, $J = 8.6$ Hz); ^{13}C NMR δ 105.1, 116.6, 128.5, 130.0, 137.3, 156.4.

¹HNMR of the known compounds

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