SUPPORTING INFORMATION

for

"Convergent Regiodirected Assembly of 2,3-Disubstituted Furans"

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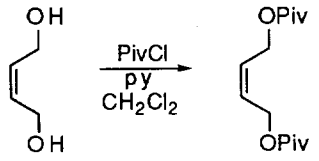
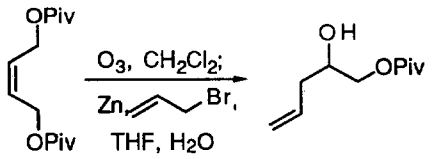
(6 Pages)



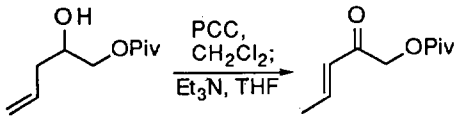
(Z)-2-Butene-1,4-diol (5.0 g, 56.7 mmol) was dissolved in dry CH_2Cl_2 (200 mL), cooled to 0 °C under N_2, and slowly treated sequentially via syringe with pivaloyl chloride (21 mL, 339 mmol) and pyridine (14 mL, 339 mmol). The reaction mixture was stirred overnight at room temperature, poured into a separatory funnel, and washed with 0.5 M $KHSO_4$ solution, brine, and water. The organic layer was dried, filtered, and concentrated to furnish 14.6 g of residual oil. A small portion of this material was purified, and the balance was directly ozonolyzed; colorless oil; IR (neat, cm^{-1}) 1732, 1481; ^1H NMR (300 MHz, $CDCl_3$) δ 5.70 (t, J = 5.0 Hz, 2 H), 4.63 (d, J = 5.0 Hz, 4 H), 1.17 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1 (2C), 128.1 (2C), 60.0 (2C), 38.6 (2C), 27.1 (6C); EI MS m/z (M^+) calcd 256.1674, obsd 256.1688.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.38; H, 9.48.



The unpurified product from above was dissolved in dry CH_2Cl_2 (250 mL), cooled to -78 °C, and treated with ozone until a blue color developed. The solvent was carefully removed under reduced pressure, and the residue was taken up in THF (250 mL) and saturated NH_4Cl solution (50 mL). This solution was stirred at 0 °C while zinc dust (14.8 g, 227 mmol) and allyl bromide (14.7 mL, 170 mmol) were introduced. After 30 min of vigorous agitation, the mixture was filtered through a pad of Celite and freed of solvent. The residue was dissolved in ether (300 mL), water (75 mL) was added, and the separated organic phase was washed with 0.5 M $KHSO_4$ solution, water, and brine prior to drying and concentration. Purification was achieved by chromatography on silica gel (elution with 15%

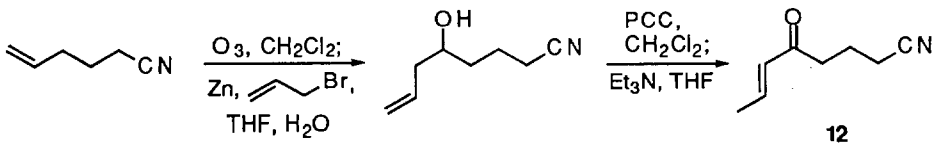
ether in petroleum ether) to give 19.4 g (91% over three steps) of the homoallylic alcohol as a colorless oil; IR (neat, cm^{-1}) 3460, 1732, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 5.86-5.72 (m, 1 H), 5.11 (d, J = 16.8 Hz, 1 H), 5.09 (d, J = 10.4 Hz, 1 H), 4.80 (dd, J = 11.4, 3.9 Hz, 1 H), 3.98 (dd, J = 11.4, 6.3 Hz, 1 H), 3.90-3.83 (m, 1 H), 2.69 (br s, 1 H), 2.32-2.18 (m, 2 H), 1.18 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 133.5, 118.2, 69.1, 67.6, 38.7, 38.0, 27.1 (3C); EI MS m/z (M^+) calcd 186.1255, obsd 186.1221.



10

The preceding alcohol (14.0 g, 75.3 mmol) in dry CH_2Cl_2 (50 mL) was added during 30 min to a stirred suspension of pyridinium chlorochromate (24.3 g, 113 mmol) and 4Å molecular sieves (25 g) in dry CH_2Cl_2 (200 mL) at 0 °C and under N_2. After 3 h of stirring at room temperature, petroleum ether (200 mL) was introduced and the mixture was filtered through a pad of silica gel. The filtrate was concentrated, redissolved in THF (200 mL), treated with triethylamine (32 mL, 225 mmol), and refluxed overnight. Removal of the volatiles in vacuo and chromatography of the residue on silica gel furnished 11.3 g (81%) of **10** as a faint yellowish oil; IR (neat, cm^{-1}) 1741, 1712, 1694, 1641; ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (dq, J = 15.8, 6.9 Hz, 1 H), 6.12 (dd, J = 15.8, 1.6 Hz, 1 H), 4.74 (s, 2 H), 1.86 (dd, J = 6.9, 1.6 Hz, 3 H), 1.21 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 177.7, 144.1, 127.4, 66.6, 38.6, 27.0 (3C), 18.3; ES MS m/z $(M + Na)^+$ calcd 185.1178, obsd 185.1170.

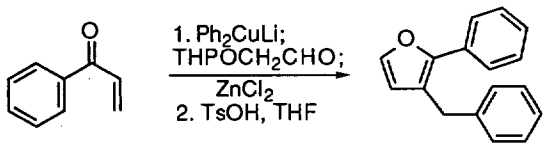
Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.94; H, 8.73.



12

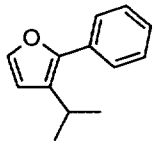
Reaction of a 1.0 g (10.5 mmol) sample of the nitrile in the predescribed manner afforded 1.26 g (87%) of the homoallylic alcohol; colorless oil; IR (neat, cm^{-1}) 3423, 2246, 1641; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83-5.68 (m, 1 H), 5.10-5.05 (m, 2 H), 3.65-3.56 (m, 1 H), 2.35 (t, J = 7.0 Hz, 2 H), 2.27-2.07 (series of m, 3 H), 1.83-1.49 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.1, 119.6, 118.1, 69.5, 41.9, 35.0, 21.6, 16.9; ES MS *m/z* $(M + Na)^+$ calcd 262.1208, obsd 262.1214.

Analogous oxidation of this material provided **12** in 68% yield; colorless oil; IR (neat, cm^{-1}) 2246, 1695, 1671, 1632; ^1H NMR (300 MHz, $CDCl_3$) δ 6.77 (dq, J = 15.8, 6.8 Hz, 1 H), 6.00 (d, J = 15.8 Hz, 1 H), 2.60 (t, J = 7.0 Hz, 2 H), 2.31 (t, J = 7.0 Hz, 2 H), 1.82 (quintet, J = 7.0 Hz, 2 H), 1.79 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 143.0, 131.2, 119.1, 37.0, 19.2, 17.8, 16.0; ES MS *m/z* $(M + Na)^+$ calcd 160.0738, obsd 160.0731.



2 **3**

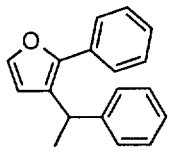
Application of the general protocol to **2** (330 mg, 2.5 mmol) yielded 286 mg (49%) of **3**: colorless oil; IR (neat, cm^{-1})1688, 1602, 1453; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72-7.63 (m, 2 H), 7.48-7.23 (series of m, 9 H), 6.30 (d, J = 1.7 Hz, 1 H), 4.08 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 141.3, 140.1, 131.3, 128.6 (3C), 128.5 (2C), 128.4, 127.2, 126.2, 125.7 (2C), 119.3, 114.2, 31.8; EI MS *m/z* (M^+) calcd 234.1045, obsd 234.1050.



Colorless oil; IR (neat, cm^{-1}) 1608, 1512, 1488, 1465; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2 H), 7.48-7.43 (m, 3 H), 7.32 (t, J = 7.3 Hz, 1 H), 6.49 (d, J = 1.8 Hz, 1 H), 3.29 (septet, J = 6.8 Hz, 1 H), 1.30 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3,

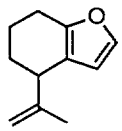
141.2, 131.8, 128.5 (2C), 128.1, 126.9, 126.0 (2C), 110.3, 24.7, 23.6 (2C); EI MS *m/z* (M^+) calcd 186.1045, obsd 186.1050.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.65; H, 7.78.



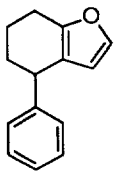
Colorless oil; IR (neat, cm^{-1}) 1601, 1511, 1485, 1449; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2 H), 7.53 (d, *J* = 1.7 Hz, 1 H), 7.48-7.27 (series of m, 8 H), 6.58 (d, *J* = 1.7 Hz, 1 H), 4.47 (q, *J* = 7.2 Hz, 1 H), 1.70 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 146.0, 141.4, 131.4, 128.5 (4C), 127.2 (3C), 126.1 (3C), 125.1, 111.8, 35.5, 23.0; ES MS *m/z* $(M + Na)^+$ calcd 249.1279, obsd 249.1286.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.08; H, 6.49.



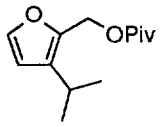
Colorless oil; IR (neat, cm^{-1}) 1646, 1507, 1446; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.8 Hz, 1 H), 6.14 (d, *J* = 1.8 Hz, 1 H), 4.82 (dd, *J* = 1.4, 0.8 Hz, 1 H), 4.72 (d, *J* = 1.4 Hz, 1 H), 3.29-3.25 (m, 1 H), 2.58 (t, *J* = 5.3 Hz, 2 H), 2.00-1.55 (series of m, 4 H), 1.69 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 147.9, 140.1, 118.8, 111.8, 110.2, 41.7, 28.6, 23.1, 21.4, 20.0; EI MS *m/z* (M^+) calcd 162.1045, obsd 162.1062.

This furan undergoes significant coloration when maintained at room temperature open to the air for 48 h.

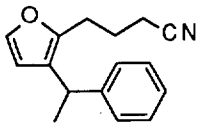


Colorless oil; IR (neat, cm^{-1}) 1601, 1507, 1453; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.15 (series of m, 6 H), 6.04 (d, *J* = 1.8 Hz, 1 H), 3.90 (dd, *J* = 7.6, 5.7 Hz, 1 H), 2.76-2.64 (m, 2 H), 2.18-2.09 (m, 1 H), 2.03-1.92 (m, 1 H), 1.88-1.77 (m, 1 H), 1.76-1.64 (m, 1 H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 151.6, 145.6, 140.4, 128.2 (2C), 127.9 (2C), 126.1, 119.3, 110.3, 40.1, 33.7, 23.1, 21.4; EI MS *m/z* (M^+) calcd 198.1045, obsd 198.1048.



Colorless liquid; IR (neat, cm^{-1}) 1731, 1506, 1480; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 1.8 Hz, 1 H), 6.28 (d, J = 1.8 Hz, 1 H), 5.02 (s, 2 H), 2.92 (septet, J = 6.9 Hz, 1 H), 1.16 (s, 9 H), 1.15 (d, J = 6.9 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 143.7, 142.3, 131.5, 109.1, 56.5, 38.7, 27.0 (3C), 24.3, 23:7 (2C); EI MS *m/z* (M^+) calcd 224.1412, obsd 224.1413.



Colorless oil; IR (neat, cm^{-1}) 2246, 1601, 1513, 1453; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.18 (series of m, 6 H), 6.38 (d, J = 1.9 Hz, 1 H), 4.01 (q, J = 7.2 Hz, 1 H), 2.76-2.67 (m, 2 H), 2.19 (t, J = 7.0 Hz, 2 H), 1.88 (quintet, J = 7.0 Hz, 2 H), 1.58 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 146.2, 140.7, 128.4 (2C), 126.9 (2C), 126.1, 124.8, 119.3, 110.1, 35.3, 24.7, 24.0, 22.4, 16.2; ES MS *m/z* $(M + Na)^+$ calcd 262.1208, obsd 262.1214.