Supporting Information for

Alkynyliodonium Salts in Organic Synthesis. Preparation of 2-Substituted-3-*p*-Toluenesulfonyldihydrofurans from 1-Hydroxybut-3-ynyliodonium Ethers via a Formal Stevens Shift of a Carbon Group.

Ken S. Feldman* and Michelle Laci Wrobleski

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

Representative experimental, and spectral data for **7a**, **7c**-**g**, and **8**

7d. Cyano(phenyl)iodonium triflate (0.13 g, 0.34 mmol) was added to a -42°C deoxygenated solution of the alkynylstannane **4d** (0.15 g, 0.34 mmol) in 3 mL of CH_2Cl_2. After 2 h the solvent was removed *in vacuo* and the white residue at -42 °C was used immediately (assume a quantitative yield of iodonium salt). To a refluxing suspension of anhydrous sodium *p*-toluenesulfinate (79 mg, 0.44 mmol) in 1 mL of THF was added the alkynyl(phenyl)iodonium triflate (0.16 g, 0.34 mmol) in 1 mL of THF at -42°C via cannula, then rinsed once with 0.2 mL of THF. The yellow suspension was allowed to reflux for 30 min, and then stirred at room temperature for 10 min. The reaction mixture was diluted with 4 mL of saturated sodium bicarbonate solution and15 mL of Et_2O. The organic layer was washed sequentially with 5 mL of H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford 0.25 g of a yellow oil. Purification of the crude material by flash chromatography on H_2O-deactivated silica gel eluting with 25% EtOAc/hexanes gave 42 mg (41%) of **7d** as a white solid: mp 98 °C (decomp.)

7a: mp 86-87 °C; IR (KBr): 2928, 2857, 1558, 1312, 1159 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 7.76 (d, *J*=8.2 Hz, 2 H), 7.32 (d, *J* = 7.9 Hz, 2 H), 4.40 (t, *J* = 10.0 Hz, 2 H), 2.78 (t, *J* = 10.0 Hz, 2 H), 2.43 (s, 3 H), 0.99 (s, 9 H), 0.36 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.7, 143.5, 138.5, 129.6, 127.3, 125.5, 72.1, 31.3, 26.8, 21.5, 17.5, -5.0. MS (CI +) 339 (MH^+, 7). Anal. Calcd for $C_{17}H_{26}O_3SSi$: C, 60.31; H, 7.74. Found: C, 60.14; H, 7.69

7c: mp 111-112 °C; IR (film): 2976, 2873, 1628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.77 (d, *J*=8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.54 (t, *J* = 6.0 Hz, 1 H), 4.43 (t, *J* = 11.0 Hz, 2 H), 3.97-3.87 (m, 2 H), 3.01-2.93 (m, 1 H), 2.78-2.70 (m, 1H), 2.43 (s, 3 H), 2.31-2.25 (m, 1 H), 2.08-1.93 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.9, 144.0, 138.5, 129.9, 127.2, 110.7, 71.5, 70.5, 69.8, 30.8, 30.5, 26.5, 21.7. MS (CI +) 295 (MH^+, 54). Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.16. Found: C, 61.20; H, 6.32.

7d: mp 98 °C (decomp.); IR (film): 2936, 2856, 1629 cm^{-1};^1H NMR (400 MHz, $CDCl_3$) 7.76 (d, *J*=8.5 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 5.09-5.06 (m, 1 H), 4.51-4.40 (m, 2 H), 4.08 (dd, *J* = 11.0, 4.0 Hz, 1 H), 3.60 (dd, *J* = 11.5, 2.5 Hz, 1 H), 2.99-2.91 (m, 1 H), 2.78-2.70 (m, 1 H), 2.44 (s, 3 H), 1.93-1.89 (m, 1 H), 1.77-1.54 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.2, 143.9, 138.4, 129.7, 127.1, 109.7, 71.5, 70.6, 68.9, 30.3, 29.4, 25.4, 23.0, 21.6. MS (CI +) 309 (MH^+, 100). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.54. Found: C, 62.46; H, 6.62.

7e: IR (film): 2934, 2871, 1622 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) 7.89 (d, *J*=8.2 Hz, 2 H), 6.79 (d, *J* = 8.7 Hz, 2 H), 5.65 (d, *J* = 3.6 Hz, 1 H), 3.87 (dt, *J* = 11.5, 3.6 Hz, 1 H), 3.69-3.42 (m, 3 H), 2.64-2.54 (m, 1 H), 2.32-2.22 (m, 2 H), 1.88 (s, 3 H), 1.71-1.45 (m, 3 H), 1.10-1.05 (m, 1 H) with overlapping 1.08 (d, *J*= 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, C_6D_6) 167.8, 143.6, 140.5, 130.1, 127.8, 111.2, 73.9, 70.3, 68.0, 33.3, 30.8, 30.2, 22.7, 21.5, 15.0. MS (CI +) 323 (MH^+, 100). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88. Found: C, 62.86; H, 6.93.

7f: IR (film): 2934, 2871, 1622 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) 7.95 (d, *J*=8.2 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 3.93-3.89 (m, 1 H), 3.68-3.53 (m, 2 H), 3.42-3.35 (m, 1 H), 2.65-2.56 (m, 1 H), 2.34-2.22 (m, 1 H), 2.01-1.87 (m, 1 H), 1.88 (s, 3 H), 1.59-1.49 (m, 2 H), 1.16-1.03 (m, 2 H) 0.92 (d, *J*= 6.4 Hz, 3 H); ^{13}C NMR (90 MHz, C_6D_6) 165.1, 143.2, 140.1, 129.7, 128.5, 113.6, 76.6, 69.8, 68.6, 32.7, 32.1, 30.8, 26.6, 21.1, 17.8. MS (CI +) 323 (MH^+, 100). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88. Found: C, 63.00; H, 6.94.

7g: mp 184-185 °C; IR (film): 2967, 2861, 1647 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) 7.93 (d, *J*=8.7 Hz, 2 H), 6.81 (d, *J* = 7.9 Hz, 2 H), 6.59 (s, 1 H), 3.83 (dd, *J* = 10.6, 4.9 Hz, 2 H), 3.61-3.51 (m, 4 H), 2.31 (t, *J* = 10.2 Hz, 2 H), 1.90-1.77 (m, 1 H) with overlapping 1.88 (s, 3 H), 0.57-0.53 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) 161.6, 143.4, 139.7, 129.8, 128.1, 113.0, 94.2, 70.3, 67.2, 30.5, 25.8, 21.1. MS (CI +) 311 (MH^+, 100). Anal. Calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.84. Found: C, 58.19; H, 6.03.

8: mp 106-107 °C; IR (film): 3091, 2929, 1607 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 7.77 (d, *J*=8.2 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.19 (t, *J* = 1.8 Hz, 1 H), 4.59 (t, *J* = 9.6 Hz, 2 H), 2.78 (dt, *J* = 9.6, 1.7 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.5, 156.3, 144.0, 137.8, 129.9, 129.7, 127.3, 117.6, 74.0, 28.1, 21.6. MS (+FAB/3NBA) 225 (MH^+, 70). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.80; H, 5.54.