SUPPORTING INFORMATION

Kishner's Reduction of 2-Furylhydrazone Gives 2-Methylene-2,3-dihydrofuran, a Highly Reactive Ene in the Ene Reaction

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Table of Contents

Materials and Methods.....	2S
Ethyl 3-(2-furyl)-2-hydroxy-propionate (4a, entry 1).....	2S
(1S)-2-(2-furyl)-1-phenylethan-1-ol ((S)-4b entry 3).....	2S
1-(2-furyl)undecan-2-ol (4c, entry 4).....	3S
(2R,3S)-4-(2-Furyl)-1,2-O-isopropylidenebutane-1,2,3-triol (4d, entry 6).....	3S
N,N-dimethyl-2-(2-furyl)ethylamine hydrogen iodide (4e, entry 7).....	3S
Diethyl 2-(2-furylmethyl)butane-1,4-dioate (4f, entry 8).....	4S
Electron donor-acceptor complex 6.....	4S
2-(4-Hydroxyphenyl)-5-methylene-2,5-dihydrofuran (5).....	4S
References.....	4S
¹ H NMR of 2.....	6S
¹ C NMR of 2.....	7S
H,C-COSY of 2.....	8S
¹ H NMR of 4a.....	9S
¹ C NMR of 4a.....	10S
¹ H NMR of (S)-4b (with 33 mol% Eu(hfc) ₃ insert).....	11S
¹ C NMR of (S)-4b	12S
¹ H NMR of (R)-4c (with 33 mol% Eu(hfc) ₃ insert).....	13S
¹ C NMR of (R)-4c	14S
¹ H NMR of 4d.....	15S
¹ C NMR of 4d.....	16S
¹ H NMR of 4e.....	17S
¹ C NMR of 4e.....	18S
¹ H NMR of 4f.....	19S
¹ C NMR of 4f.....	20S
¹ H NMR of 6.....	21S
¹ C NMR of 6.....	22S
¹ H NMR of 5.....	23S
¹ C NMR of 5.....	24S

Materials and Methods. All reactions were carried out under Ar. All glassware used in the preparation and reactions of **2** was washed with aqueous base. IR spectra were obtained on a FT-IR spectrometer. The ^1H NMR and ^{13}C NMR were recorded at 400 MHz and 100 MHz, respectively. All chemical shifts in the ^1H NMR are reported in ppm relative to TMS ($\delta = 0.00$ ppm) or C_6HD_5 ($\delta = 7.15$ ppm) and in the ^{13}C NMR are reported in ppm relative to CDCl_3 ($\delta = 77.0$ ppm), or C_6D_6 ($\delta = 128.0$ ppm). Flash chromatography was performed on 60 Å silica gel (40-75 μm). Diethyl ether, methylene chloride, and tetrahydrofuran were purified on alumina using a Sol-Tech solvent purification system. 2,3-*O*-isopropylidene-*D*-glyceraldehyde was prepared from 1,2:5,6-diisopropylidene-*D*-mannitol.[†] Pure ethyl glyoxylate was prepared from the commercially available toluene solution of the polymer by the following procedure: the toluene was distilled from the polymer under vacuum at room temperature and then the polymer was heated with P_4O_{10} to 60-100°C under vacuum (5mm) to give pure ethyl glyoxylate. 1,4-Benzoquinone was sublimed before use. (*S*)-BINOL, ytterbium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) ($\text{Yb}(\text{fod})_3$), ytterbium tris(3-(heptafluoropropylhydroxymethylene)-(+)-camphorate ($\text{Yb}(\text{hfc})_3$), and kaolin were purchased from commercial sources. Moist potter's clay was purchased from a local arts supply store.

Ethyl 3-(2-furyl)-2-hydroxy-propionate² (4a; entry 1). 2-Methylene-2, 3-dihydrofuran (2.0 mL of a 1:1.3 mixture of 2:2-methylfuran, approximately 9.8 mmol of **2**) was added dropwise to a solution of ethyl glyoxalate (0.538 g, 5.27 mmol) in CH_2Cl_2 (10 mL) at 0°C. After stirring for 1 h at 0°C, the volatiles were removed on the rotary evaporator. The crude product was purified by flash chromatography (20 g silica gel; 10% EtOAc in hexanes) to give **4a** (0.861 g, 89%) as a light yellow oil. IR 3536, 1734 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (dd, $J = 0.9, 1.8$ Hz, 1H), 6.30 (dd, $J = 1.8, 2.9$ Hz, 1H), 6.13 (dd, $J = 0.7, 3.3$ Hz, 1H), 4.45 (m, 1H), 4.25 (m, 2H), 3.15 (dd, $J = 4.6, 15.0$ Hz, 1H), 3.05 (dd, $J = 6.0, 15.2$ Hz, 1H), 2.88 (br d, $J = 5.1$ Hz, 1H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 150.5, 141.6, 110.2, 107.6, 69.2, 61.7, 33.1, 14.0.

(1*S*)-2-(2-furyl)-1-phenylethan-1-ol³ (S-4b, entry 3). In a 25 mL Schlenk flask fitted with a magnetic stirrer, 4 Å molecular sieves (5.0 g) were dried under vacuum at 130-140°C for 35 min. Ether (10 mL), (*S*)-1,1'-bi-naphthol (0.286 g, 1.00 mmol), and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (0.143 mL, 0.137 g, 0.483 mmol) were added and the mixture was refluxed for 1 h. After cooling to room temperature, benzaldehyde (0.510 mL, 0.536 g, 5.05 mmol) was added and stirred at room temperature for 5 min. 2-Methylene-2,3-dihydrofuran (3.0 mL of a 1:3 mixture of 2:2-methylfuran, approximately 8.4 mmol) was then added over 5 min at room temperature. The reaction mixture was stirred for an additional 20 min. Saturated sodium bicarbonate solution (1 mL) was added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered through a Celite bed, which was washed with additional ether (50 mL). The ether solution was washed with 1.0 M NaOH (75 mL), dried over Na_2SO_4 , and the volatiles were removed on the rotary evaporator. The crude product was purified by flash chromatography (25 g silica gel; 10% EtOAc in hexanes) to give **4b** (0.864 g, 91% yield, 54% ee) as a yellow oil. The ^1H and ^{13}C NMR are given in the text of the paper. The enantiomeric excess was determined by the use of the chiral shift reagent $\text{Eu}(\text{hfc})_3$. The

ortho-protons of the phenyl ring for the two enantiomers resonate as doublets ($J = 7.7$ Hz) at δ 8.63 for (1*S*)-2-(2-furyl)-1-phenylethan-1-ol and δ 8.53 for (1*R*)-2-(2-furyl)-1-phenylethan-1-ol (0.054 M of 2-(2-furyl)-1-phenylethan-1-ol with 24 mol% Eu(hfc)₃ in CDCl₃). The straightforward analysis of the ¹H NMR spectra of the (+)-MTPA esters⁴ lead the assignment of the major enantiomer as *S*. Partial ¹H NMR (400 MHz, CDCl₃) of the major (+)-MTPA ester: δ 6.29 (dd, 1H, $J = 1.8, 3.0$ Hz, H₄) and 6.07 (d, 1H, $J = 3.1$ Hz, H₃); partial ¹H NMR (400 MHz, CDCl₃) of the minor (+)-MTPA ester: δ 6.20 (dd, 1H, $J = 1.8, 3.0$ Hz, H₄), and 5.87 (d, 1H, $J = 3.1$ Hz, H₃).

1-(2-furyl)undecan-2-ol (4c, entry 4). To ZnCl₂ (0.339 g, 2.47 mmol) in Et₂O (5 mL) was added decanal (0.46 mL, 0.38 g, 2.5 mmol) in CH₂Cl₂ (5 mL). 2-Methylene-2,3-dihydrofuran (0.75 mL of a 1:1.3 mixture of 2:2-methylfuran; approximately 3.7 mmol of **2**) was then added over 1 min. The reaction mixture was allowed to stir for 30 minutes and then water (5 mL) was added to quench the reaction. The reaction mixture was transferred to a separatory funnel with CH₂Cl₂ (20 mL), the organic phase was separated, and the aqueous phase was washed extracted with additional CH₂Cl₂ (2 x 20 mL). The combined organic phases were washed with brine (2 x 25 mL), dried over NaSO₄, and volatiles were removed on the rotary evaporator. The crude product was purified by flash chromatography (30 g of silica gel; 10% EtOAc in hexanes) to give **4c** (0.458 g, 78% yield) as a clear oil. The ¹H and ¹³C NMR spectra are given in the text of the paper.

(2*R*,3*S*)-4-(2-Furyl)-1,2-*O*-isopropylidenebutane-1,2,3-triol (4d, entry 6). To a solution of 2,3-*O*-isopropylidene-*D*-glyceraldehyde¹ (0.53 g, 4.1 mmol) in CH₂Cl₂ (10 mL) at 0°C was added 2-methylene-2,3-dihydrofuran (1.5 mL of a 1:1.3 mixture of 2:2-methylfuran, approximately 7.3 mmol of **2**) and Yb(fod)₃ (0.043 g, 0.041 mmol). The reaction mixture was stirred for 1 h at 0°C and then 1 h at room temperature. The volatiles were removed on the rotary evaporator and the crude product was purified by flash chromatography (25 g silica gel; 10% EtOAc in hexanes → 20% EtOAc in hexanes) to give **4d** (0.810 g, 93% yield, 65% de) as a clear oil. IR 3462, 1598 cm⁻¹. Major diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 7.33 (t, $J = 0.9$ Hz, 1H), 6.30 (m, 1H), 6.12 (d, $J = 2.6$ Hz), 3.90-4.08 (m, 4H), 2.92 (dd, $J = 4.2, 15.2$ Hz, 1H), 2.79 (dd, $J = 7.5, 15.2$ Hz), 2.28 (br s, 1H), 1.42 (s, 3H), 1.35 (s, 3H); ¹³C NMR (100 MHz) δ 151.8, 141.7, 110.4, 109.2, 107.3, 77.8, 70.5, 65.5, 32.0, 26.6, 25.3. Minor diastereomer: Partial ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, $J = 0.9$ Hz), 3.83-3.89 (m, 1H), 3.68 (m, 1H); 1.43 (s, 3H), 1.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 141.5, 110.4, 109.4, 107.2, 78.0, 70.8, 65.8, 32.6, 26.5, 25.2. Anal. Calcd for C₁₁H₁₆O₄: C, 62.25; H, 7.60. Found: C, 61.78; H, 7.76. The stereochemical assignment was based by comparing the coupling constants of the methylene protons of the major product above with the related known diastereomers (2*R*,3*R*)-4-(phenyl)-1,2-*O*-isopropylidenebutane-1,2,3-triol and (2*R*,3*S*)-4-(phenyl)-1,2-*O*-isopropylidenebutane-1,2,3-triol.⁵

N,N-Dimethyl-2-(2-furyl)ethylamine hydrogen iodide (4e, entry 7). To Eschenmoser's salt (0.252 g, 1.36 mmol) in CH₂Cl₂ (5 mL) was added **2** (0.50 mL of a 1:1.3 mixture of 2:2-methylfuran; approximately 2.4 mmol of **2**). The mixture was allowed to stir for 3 h and the volatiles were removed on the rotary evaporator. The crude solid was

recrystallized from EtOAc (25 mL) to give **4e** (0.270 g, 74% yield) as a light pink solid: mp 103-104.5⁰C; IR 2580, 1603 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.33 (d, *J* = 1.8 Hz, 1H), 6.31 (dd, *J* = 2.0 Hz, 3.1 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 3.42 (m, 2H), 3.34 (m, 2H), 2.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 142.2, 110.6, 107.9, 55.8, 43.2, 23.4. Anal. Calcd for C₈H₁₄INO: C, 35.97; H, 5.28. Found: C, 36.28; H, 5.37.

Diethyl 2-(2-furylmethyl)butane-1,4-dioate (4f, entry 8). Diethyl maleate (0.50 mL, 0.53 g, 3.1 mmol), 2-methylene-2,3-dihydrofuran (1.0 mL of 1:1.3 mixture of 2:2-methylfuran, approximately 4.9 mmol), and sodium acetate (0.12 g, 1.5 mmol) in *m*-xylene (5 mL) were heated to 150–160⁰C in a sealed tube for 65 hours. After cooling to room temperature, the solvent was removed by vacuum distillation. The crude material was purified by flash chromatography (20 g silica gel; hexanes → 5% EtOAc in hexanes) to give **4f** (0.438 g, 56% yield) as a light yellow oil. IR 2984, 1730, 1179 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, *J* = 0.7, 1.8 Hz, 1H), 6.26 (dd, *J* = 1.8, 2.9 Hz, 1H), 6.04 (br d, *J* = 2.7 Hz, 1H), 4.12 (m, 4H), 3.17 (m, 1H), 3.03 (dd, *J* = 6.2, 15.0 Hz, 1H), 2.88 (dd, *J* = 8.1, 15.0 Hz, 1H), 2.68 (dd, *J* = 8.8, 16.9 Hz, 1H), 2.45 (dd, *J* = 5.3, 16.7 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 171.6, 152.1, 141.6, 129.9, 110.1, 107.0, 60.7, 60.5, 40.6, 35.1, 29.8, 14.10, 14.08. Anal. Calcd for C₁₁H₁₆O₄: C, 61.41; H, 7.13. Found: C, 61.24; H, 7.28.

Electron donor-acceptor complex 6. To a slurry of 1,4-benzoquinone (2.20 g, 20.4 mmol) in benzene (5 mL) was added **2** (2.0 mL of a 1:1.3 mixture of 2:2-methylfuran, approximately 9.8 mmol of **2**). After stirring for 24 h, hexane (10 mL) was added and stirred for an additional 30 min. The reaction mixture was filtered, washing the product with hexane (5 x 10 mL) to give **6** as red crystals (2.13 g; 73% yield): mp 100-102⁰C (lit.⁴ 105⁰C); IR (CH₂Cl₂) 3584, 1658, 1591 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.01 and 6.47 (AA'BB', 4H), 6.14 (br s, 1H), 5.90 (s, 4H), 5.85 (d, *J* = 5.8 Hz, 1H), 5.68 (d, *J* = 5.9 Hz, 1H), 4.56 (br s, 1H), 4.15 (br s, 1H; exchanges with D₂O), 4.00 (br s, 1H); ¹³C NMR (100 MHz, C₆D₆) δ 186.8 (C), 162.7 (C), 151.9 (C), 151.3 (C), 135.7 (CH), 131.1 (CH), 129.4 (CH), 119.0 (CH), 116.1 (CH), 107.7 (CH), 84.7 (CH₂).

2-(4-Hydroxyphenyl)-5-methylene-2,5-dihydrofuran (5). Charge transfer complex **6** (0.500 g, 1.68 mmol) was dissolved in ethyl acetate (5 mL), absorbed on silica gel (5 g), and the solvent was removed on the rotary evaporator. Flash chromatography (20 g of silica gel; 10% EtOAc in hexanes → 20% EtOAc in hexanes) gave 1,4-benzoquinone (0.113 g, 63% yield; some was lost due to sublimation during solvent removal) and impure **5** (0.243 g, 76% yield) as an air- and thermally-sensitive colorless oil that became orange. IR (C₆H₆) 3584, 1669, 1638, 1587 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.01 and 6.47 (AA'BB', 4H), 6.14 (br s, 1H), 5.85 (d, *J* = 5.8 Hz, 1H), 5.68 (d, *J* = 5.9 Hz, 1H), 4.56 (br s, 1H), 4.00 (br s, 1H), 3.72 (br s, 1H; exchanges with D₂O); ¹³C NMR (100 MHz, C₆D₆) δ 162.7, 151.9, 151.3, 131.0, 129.4, 119.0, 116.2, 107.8, 84.7.

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