

*Supporting Information for*

**The *gem*-Dialkyl Effect in Electron Transfer Reactions: Rapid Synthesis of Seven-Membered Rings Through an Electrochemical Annulation**

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## General Experimental

All reactions were carried out in flame-dried glassware under an atmosphere of argon unless otherwise noted. Tetrahydrofuran was freshly distilled from Na/benzophenone. Mixtures of TMSCl and Et<sub>3</sub>N refer to the supernatant liquid from a centrifuged 1:1 v:v solution made in a flame dried distillation receiver under argon. These solutions can be kept up to 3 days in a -20°C freezer. All commercially available enones were distilled prior to use and kept in a freezer under an atmosphere of argon. Copper (I) iodide was either purchased at 99.999% purity (Aldrich) or purified by Soxhlet extraction with CH<sub>2</sub>Cl<sub>2</sub>. Electrolysis reactions were carried out as previously reported with alternating stainless steel cathodes and carbon anodes. No attempts were made to exclude air or water from these reactions. NMR spectra were either obtained on a Bruker 300 or a Varian Inova 500. Cyclic voltammogram data were obtained from 1mM solutions of the desired crude enolethers in freshly distilled acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The experimental reference electrode was a AgCl-coated Ag wire prepared by anodic electrolysis of a Ag wire in HCl solution. All potentials supplied here, however, are referenced to the ferrocene/ferrocenium reference couple. This was accomplished by adding cobaltocenium hexafluorophosphate to the electrochemical solution as an internal standard and then altering the measured potential by the difference between the [FeCp<sub>2</sub>]<sup>0/+</sup> and [CoCp<sub>2</sub>]<sup>+0</sup> potentials in these media. Half-wave potentials were taken to be the mid-point of the oxidation peak in each case and rounded to the nearest 0.01mV.

Chromatography of the annulated furans *must* be performed through deaerated silica gel. This can be accomplished by placing the silica gel into an Erlenmeyer flask with the desired elution solvent. A glass pipette attached to an argon source was placed into the mixture and argon was bubbled through the silica gel for 30 minutes with mixing every 5 minutes. A column with the same volume of the elution solvent as in the Erlenmeyer flask (also previously degassed with argon) was constructed and nitrogen was passed over the solvent for fifteen minutes. The degassed silica gel mixture was poured into the column and any residual silica gel was washed out of the Erlenmeyer flask with the solvent *from the column*. Once all of the silica gel is in the column, the total volume of elution solvent is passed through 3 times. The crude material is loaded, and fractions collected. To minimize oxidation of the compounds collected from the column, all of the fractions containing product was be collected within a few minutes, concentrated and placed under argon.

**General Cuprate Procedure:**

A solution of 3-(3-furyl)-propyl bromide (**5**) (1.0g, 5.2 mmol) in THF (5.5 mL) was purged with argon for 10 min. This solution was then added to a flask containing Mg turnings (0.132 g, 5.5 mmol). After 2.5 h the majority of the Mg had dissolved and a clear dark solution had formed. The solution was cooled to 0°C and CuI (0.165 g, 0.87mmol) was added. After stirring for 5 min the turbid black solution was cooled to -78°C. A mixture of TMSCl:Et<sub>3</sub>N (5.5 mL) was added, followed by N,N,N,N-tetramethylethylenediamine (0.90mL, 5.5 mmol). Next, the addition of the enone (4.5 mmol) produced a bright yellow solution. The mixture was allowed to warm to rt over 5 h and placed into a refrigerator overnight. The black mixture was then poured into an ice-cold mixture of pentane (100 mL) and saturated aqueous NH<sub>4</sub>Cl (50 mL). The pentane layer was separated and washed with NaHCO<sub>3</sub>, then brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent provided the crude enoether (1.2 g).

**Modified cuprate procedure**

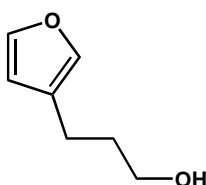
To 1.0 mL of a 1M Grignard reagent (purchased from commercial sources) was added 1.0 mL of THF and cooled to 0°C. CuX (20 mol %) was then added in one portion and the dark solution was allowed to stir at 0°C for an additional 15 minutes. The reaction was cooled to -78°C and 1.0 mL of TMSCl/Et<sub>3</sub>N was carefully added down the side of the reaction flask. Next, TMEDA (1mmol, 0.16 mL) was added followed by a solution containing enone **10** (100 mg, 0.5 mmol) in 0.5 mL of THF. The dark solution was stirred at -78°C for 4 hours and allowed to warm to room temperature. The mixture was placed into a -20°C freezer overnight. The black mixture was then poured into an ice-

cold mixture of hexanes (25 mL) and saturated aqueous  $\text{NH}_4\text{Cl}$  (20 mL). The hexanes layer was separated and washed with  $\text{NaHCO}_3$ , then brine, and dried over  $\text{Na}_2\text{SO}_4$ . Removal of solvent provided the crude enolether.

### General electrolysis procedure

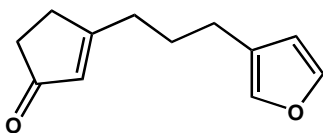
A 50-mL beaker was charged with the crude enolether (0.69 mmol) and 34.5 mL of an electrolyte solution (4:1 MeCN:2-propanol, 0.1M  $\text{LiClO}_4$ , and 0.08M 2,6-lutidine) and stirred until homogeneous. An electrode system consisting of alternating plates of carbon (anode) and steel (cathode) was inserted and charged with a constant current of 22.0 mA (current density =  $1\text{mA}/\text{cm}^2$ ). The reaction was monitored by TLC every 30 minutes until complete. Once complete, the volatiles were removed under vacuum, and the crude material was dissolved in ether (40 mL) and washed with 1 M HCl. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2x25 mL), and the combined organic phases were washed with water,  $\text{NaHCO}_3$ , brine and dried over  $\text{Na}_2\text{SO}_4$ . The crude material was concentrated *in vacuo* and chromatographed *through degassed silica gel* (20:1 hexanes:ethyl acetate) to provide the desired compounds as colorless oils. Typical amounts of charged passed ranged from 3.5-4.4 F/mol. The electrolysis reactions could also be carried out at  $40^\circ\text{C}$ . Although not accompanied by a large increase in yield, reactions at this higher temperature occurred with less polymeric material produced at the electrode surface and slightly increased the current efficiency.

### 3-Furan-3-yl-propan-1-ol



A solution of *n*-BuLi (33.0 mmol, 13.2 mL, 2.5M in hexanes) was added dropwise to a solution of 3-bromofuran (30 mmol, 4.41 g) in 30 mL of THF at -78°C over 30 minutes. The reaction was allowed to mix for 45 minutes and trimethylene oxide (33 mmol, 1.91 g) added via syringe. After 5 minutes, BF<sub>3</sub>·OEt<sub>2</sub> (33 mmol, 4.1 mL) was added slowly over 30 minutes, keeping the reaction temperature between -70°C and -78°C. The reaction was kept at -78°C for 5 hours and quenched with 100 mL of sat. NaHCO<sub>3</sub> (added dropwise via addition funnel over 1 hour). The mixture was allowed to warm to room temperature overnight. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with 40 mL of sat NaHCO<sub>3</sub>, water and brine. The crude product was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Vacuum distillation yielded 2.27 g (61%) of 3-furan-3-yl-propan-1-ol as a colorless oil with spectral data matching previous reports.

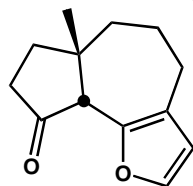
### 3-(3-furan-3-yl-propyl)-cyclopent-2-one (10)



To a degassed solution of bromide (**5**) (5 mmol, 945 mg) in THF (5 mL) was added magnesium turnings (5 mmol, 122 mg). The reaction was allowed to stir for 2 hours, then cooled to 0°C. A solution of 3-ethoxy-2-cyclopenten-1-one (4 mmol, 504 mg) in 5 mL of THF was then added dropwise and the bright orange solution was stirred for 2 hours at 0°C and 2 hours at 25°C. The reaction was quenched by adding 20 mL of 1M HCl and stirred for 4 hours. The aqueous layer was extracted twice with 50 mL of EtOAc. The combined organic layers were washed with 20 mL of saturated NaHCO<sub>3</sub>, 20 mL of water

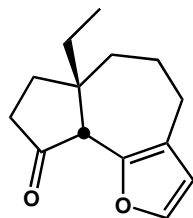
and 20 mL of brine. After drying over sodium sulfate and concentrating, the crude enone was subjected to flash silica gel chromatography (5:1 Hex:EtOAc  $\rightarrow$  1:1 Hex:EtOAc) to provide (**10**) as a pale yellow oil (2.84 mmol, 504 mg, 71%) which solidified in a -20°C freezer. IR (neat)  $\nu_{\text{max}}$  2930, 1667, 1622, 1251  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.37 (dd,  $J=2.9$  Hz,  $J=1.7$  Hz, 1H), 7.23 (s, 1H), 6.27 (d,  $J=2.8$  Hz, 1H), 5.96 (s, 1H), 2.57 (m, 2H), 2.49 (t,  $J=7.6$  Hz, 2H), 2.44 (t,  $J=7.6$  Hz, 2H), 2.40 (m, 2H), 1.86 (pentet,  $J=7.6$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  210.3, 182.7, 143.2, 139.2, 129.8, 124.3, 111.0, 35.5, 33.1, 31.8, 27.5, 24.6; EI-HRMS  $m/z$  calculated for  $\text{C}_{12}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ): 190.0994, found 190.0980.

**6a-methyl-5,6,6a,7,8,9a-hexahydro-4H-azuleno[4,5-*b*]furan-9-one (8b)**



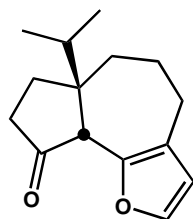
Silica gel chromatography provided **8b** as a colorless oil, which solidified in a -20°C freezer. IR (neat)  $\nu_{\text{max}}$  2930, 1715, 1631, 1505, 1251, 1107  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.28 (d,  $J=1.7$  Hz, 1H), 6.18 (d,  $J=1.7$  Hz, 1H), 3.37 (s, 1H), 2.49-2.55 (m, 1H), 2.43 (ddd,  $J=8.7$  Hz, 2.7 Hz, 1.0 Hz, 1H), 2.41 (dd,  $J=10.6$  Hz, 8.4 Hz, 1H), 2.31-2.36 (m, 1H), 1.84-1.99 (m, 2H), 1.70-1.72 (m, 4H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  215.4, 145.3, 141.3, 121.9, 113.4, 62.0, 40.2, 39.3, 37.6, 35.1, 26.1, 25.9, 22.5; EI-HRMS  $m/z$  calculated for  $\text{C}_{13}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ ): 204.1150, found 204.1137

**6a-ethyl-5,6,6a,7,8,9a-hexahydro-4H-azuleno[4,5-*b*]furan-9-one (12a)**



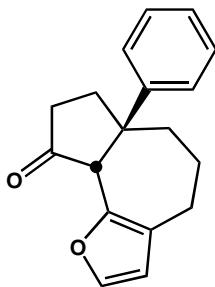
Isolated as a colorless oil, which solidified in a  $-20^{\circ}\text{C}$  freezer. IR (neat)  $\nu_{\text{max}}$  2933, 1717, 1630, 1505, 1107  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.29 (d,  $J=1.7$  Hz, 1H), 6.19 (d,  $J=1.7$  Hz, 1H), 3.62 (s, 1H), 2.52 (dt,  $J=15.5$  Hz, 3.5 Hz, 1H), 2.32-2.44 (m, 2H), 1.85-1.94 (m, 4H), 1.66-1.70 (m, 2H), 1.55-1.58 (m, 2H), 1.44-1.50 (m, 1H), 0.92 (t,  $J=7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  215.6, 145.4, 141.4, 121.8, 113.4, 61.8, 43.2, 35.3, 34.8, 34.0, 30.6, 26.2, 21.9, 8.2; EI-HRMS  $m/z$  calculated for  $\text{C}_{14}\text{H}_{18}\text{O}_2$  ( $\text{M}^+$ ): 218.1307, found 218.1293.

**6a-isopropyl-5,6,6a,7,8,9a-hexahydro-4H-azuleno[4,5-b]furan-9-one (12b)**



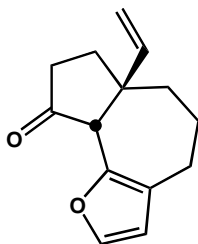
Isolated as a colorless oil, which solidified in a  $-20^{\circ}\text{C}$  freezer. IR (neat)  $\nu_{\text{max}}$  2930, 1715, 1628, 1509, 1111  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.26 (d,  $J=1.7$  Hz, 1H), 6.18 (d,  $J=1.5$  Hz, 1H), 3.62 (s, 1H), 2.34-2.44 (m, 3H), 2.49 (dt,  $J=15.8$  Hz,  $J=4.4$  Hz, 1H), 1.99-2.07 (m, 2H), 1.72-1.82 (m, 1H), 1.53-1.66 (m, 3H), 0.96 (d,  $J=2.9$  Hz, 3H), 0.82 (d,  $J=2.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  206.0, 145.6, 141.3, 121.4, 113.4, 58.7, 40.5, 35.6, 34.6, 28.6, 26.2, 21.4, 17.5, 17.0; EI-HRMS  $m/z$  calculated for  $\text{C}_{15}\text{H}_{20}\text{O}_2$  ( $\text{M}^+$ ): 232.1463, found 232.1450.

**6a-phenyl-5,6,6a,7,8,9a-hexahydro-4*H*-azuleno[4,5-*b*]furan-9-one (12c)**



Isolated as a colorless oil, which solidified in a -20°C freezer. IR (neat)  $\nu_{\max}$  2918, 2847, 1717, 1630, 1499, 1107  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.40 (d,  $J$ = 1.7 Hz, 1H), 7.32 (t,  $J$ = 7.3 Hz, 2H), 7.22 (t,  $J$ = 7.3 Hz, 1H), 7.18 (m, 2H), 6.20 (d,  $J$ = 1.7 Hz, 1H), 4.06 (s, 1H), 2.51-2.57 (m, 2H), 2.46 (dt,  $J$ = 16.4 Hz, 3.7 Hz, 1H), 2.38-2.43 (m, 1H), 2.26-2.30 (m, 1H), 2.17-2.25 (m, 1H), 1.97 (dd,  $J$ =14.4 Hz, 1.7 Hz, 1H), 1.56-1.62 (m, 1H), 1.20-1.28 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  214.5, 146.4, 145.5, 141.3, 129.1, 128.4, 128.3, 126.3, 126.2, 122.1, 113.4, 58.9, 47.7, 40.0, 37.3, 34.6, 25.9, 22.4; EI-HRMS  $m/z$  calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2$  ( $\text{M}^+$ ): 266.1307, found 266.1293.

**6a-vinyl-5,6,6a,7,8,9a-hexahydro-4*H*-azuleno[4,5-*b*]furan-9-one (12d)**

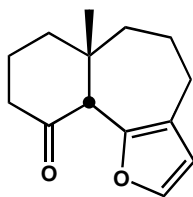


Isolated as a colorless oil, which solidified in a -20°C freezer. IR (neat)  $\nu_{\max}$  2933, 1717, 1630, 1220, 1107  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.32 (d,  $J$ = 1.7 Hz, 1H), 6.24 (d,  $J$ = 1.7 Hz, 1H), 5.77 (dd,  $J$ = 11.1 Hz, 17.2 Hz, 1H), 5.15 (d,  $J$ = 11.1 Hz, 1H), 5.06 (d,  $J$ =17.1



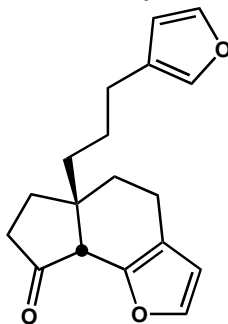
Hz, 1H), 3.64 (s, 1H), 2.45-2.61 (m, 2H), 2.15-2.31 (m, 2H), 1.71-1.91 (m, 4H), 1.51-1.65 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$ : 215.6, 147.2, 144.3, 142.9, 117.3, 114.9, 110.1, 53.5, 45.7, 39.5, 33.0, 31.1, 23.4, 19.0; EI-HRMS  $m/z$  calculated for  $\text{C}_{14}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ ): 216.1150, found 216.1136.

**6a-methyl-4,5,6,6a,7,8,9,10a-octahydro-benzo[6,7]cyclohepta[1,2b]furan-10-one (12e)**



IR (neat)  $\nu_{\text{max}}$  2931, 1711, 1622, 1500, 1110  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.21 (d,  $J=1.7\text{Hz}$ , 1H), 6.21 (d,  $J=1.7\text{Hz}$ , 1H), 3.63 (s, 1H), 2.38-2.52 (m, 4H), 1.95-2.04 (m, 2H), 1.79-1.87 (m, 2H), 1.70-1.77 (m, 2H), 1.47 (dd,  $J=14.5\text{Hz}, 5.9\text{Hz}$ , 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  208.4, 147.4, 140.2, 122.1, 113.4, 61.7, 41.6, 41.3, 40.5, 38.4, 27.7, 25.6, 23.0, 22.0; EI-HRMS  $m/z$  calculated for  $\text{C}_{14}\text{H}_{18}\text{O}_2$  ( $\text{M}^+$ ): 218.1307, found 218.1293.

**5a-(3-furan-3-yl-propyl)-4,5,5a,6,7,8a-hexahydro-1-oxa-as-indacen-8-one (14)**



Isolated as a viscous colorless oil. IR (neat)  $\nu_{\text{max}}$  2933, 1717, 1630, 1505, 1107  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.35-7.36 (m, 2H), 7.21-7.22 (m, 1H), 6.27 (s, 1H), 6.22 (d,  $J=1.6\text{Hz}$ , 1H), 3.03 (s, 1H), 2.39-2.47 (m, 6H), 1.97 (ddd,  $J=13.2\text{Hz}, 7.9\text{Hz}, 5.1\text{Hz}$ , 1H),

1.83-1.89 (m, 1H), 1.75 (dt,  $J$ = 13.7 Hz, 4.4 Hz, 1H), 1.57-1.69 (m, 4H) 1.37-1.44 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  215.4, 145.2, 143.1, 142.9, 139.1, 124.9, 116.9, 111.0, 110.2, 55.0, 43.4, 37.4, 35.5, 31.0, 28.7, 25.5, 24.5, 19.0; EI-HRMS  $m/z$  calculated for  $\text{C}_{18}\text{H}_{20}\text{O}_3$  ( $\text{M}^+$ ): 284.1412, found 284.1399.

