

Connecting the Dots: Using Sunlight to Drive Electrochemical Oxidations

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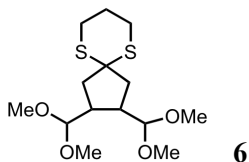
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Supporting Information

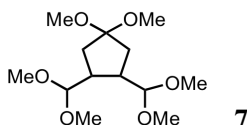
General procedure for the electrolysis reactions:

In a flame-dried three-neck round bottom flask, the substrate was dissolved in an anhydrous MeOH or 20% MeOH/CH₂Cl₂ solution (0.03 M, 1.0 equiv) with 2,6-lutidine (6.0 equiv) and either LiClO₄ or Et₄NOTs as electrolyte. The reaction flask was equipped with a reticulated vitreous carbon anode (100 PPI) and either a carbon rod or Pt wire cathode. Photovoltaic cells (purchased from Edmund Scientific, a division of VWR Education) were hooked in series based on amount of current required for the electrochemical reaction. The cells were incorporated into the electrochemical circuit and a multimeter was connected to the cathodic lead to measure the current. The photovoltaic cells were exposed to light from a plant lamp (Philips 120W agro-lite) resulting in a constant current being passed through the solution. The reaction was monitored by TLC for loss of starting material. When Et₄NOTs was used as electrolyte, the reaction was concentrated *in vacuo* upon completion. The residue was then diluted with diethyl ether, filtered to remove the electrolyte, concentrated under reduced pressure, and then chromatographed through a silica gel column to afford the product. When LiClO₄ was used as electrolyte, the solution was diluted with ether and then washed with water and brine. The organic layer was dried over MgSO₄, filtered, and concentrated. The residue was chromatographed as described above.

Spectral data:

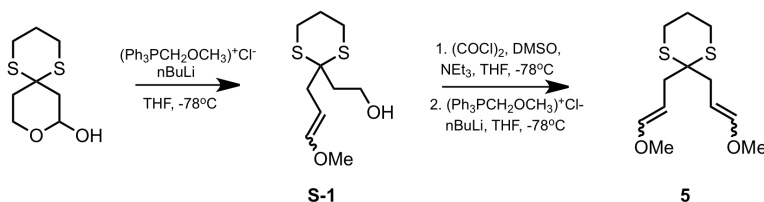


¹H NMR (300 MHz, CDCl₃) δ 4.50 (d, *J*=5.6 Hz, 0.4H), 4.43 (d, *J*=4.6 Hz, 1.6H), 3.39 (d, *J*=2.2 Hz, 9.6H), 3.35 (s, 2.4H), 2.93-2.84 (m, 4H), 2.64 (dt, *J*=12.8, 6.3 Hz, 0.4H), 2.45-2.26 (m, 3.6H), 2.19 (dd, *J*=13.5, 7.0 Hz, 2H), 2.04-1.93 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ 107.8, 55.1, 55.0, 54.1, 43.7, 42.5, 28.8, 25.7; IR (neat/NaCl) 2936, 2827, 1443, 1371, 1187, 1136, 1064, 941 cm⁻¹; ESI HRMS *m/z* (M+Na)⁺ calcd 345.1170, found 345.1177.



^1H NMR (300 MHz, CDCl_3) δ 4.29 (d, $J=5.7$ Hz, 2H), 3.36 (s, 12H), 3.18 (s, 6H), 2.20 (dt, $J=11.7, 5.8$ Hz, 2H), 1.88 (d, $J=7.6$ Hz, 4H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 110.4, 107.6, 54.7, 54.4, 49.5, 41.3, 34.6; IR (neat/ NaCl) 2941, 2826, 1443, 1369, 1327, 1057, 963 cm^{-1} ; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 301.1627, obsd 301.1633

Substrate synthesis:



Synthesis of S-1: To a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (12.3 g, 36.0 mmol) in THF (90 mL) at 0 °C was added *n*-BuLi (1.6 M, 22.5 mL) in a dropwise fashion. The dark red mixture was stirred for 30 min at 0 °C. A solution of dithiane lactol (2.47 g, 12.0 mmol) in THF (10 mL) was added over a period of 5 min. The reaction mixture was allowed to warm to room temperature, stirred overnight, and then quenched with a sat. brine solution. The aqueous layer was extracted three times with diethyl ether. The combined organic extracts were dried over Na_2SO_4 , filtered, concentrated *in vacuo*, and purified by silica gel column chromatography (hexane:ethyl acetate = 1:1, slurry-packed with 1% Et_3N) to afford alcohol enol ether S-1 (2.42 g, 10.3 mmol) in 86% yield as a 70:30 mixture of *trans* and *cis* isomers. ^1H NMR (CDCl_3 , 300 MHz) δ 6.37 (d, $J=12.6$ Hz, 0.7H), 6.05 (d, $J=6.2$ Hz, 0.3H), 4.76 (dt, $J_d=12.6, J_t=7.6$ Hz, 0.7H), 4.50 (q, $J=6.2$ Hz, 0.3H), 3.84 (q, $J=6.1$ Hz, 0.6H), 3.85 (q, $J=6.1$ Hz, 1.4H), 3.61 (s, 0.9H), 3.55 (s, 2.1H), 2.98-2.77 (m, 4H), 2.75 (d, $J=7.5$ Hz, 0.6H), 2.57 (d, $J=7.4$ Hz, 1.4H), 2.41 (t, $J=6.2$ Hz, 0.3H), 2.36 (t, $J=6.1$ Hz, 0.7H), 2.21 (t, $J=6.1$ Hz, 2H), 2.07-1.89 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 150.0, 148.8, 100.3, 96.4, 59.7, 56.2, 52.2, 40.3, 39.9, 38.3, 33.9, 26.4, 25.2; IR (neat/ NaCl) 3420, 2933, 2904, 2830, 1652, 1443, 1422, 1236, 1208, 1157, 1108, 1042, 936 cm^{-1} ; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 257.0646, obsd 257.0654.

Synthesis of 5: To a 0 °C solution of (methoxymethyl)triphenylphosphonium chloride (12.4 g, 36.1 mmol) in THF (70 mL) was added *n*-BuLi (1.6 M, 22.8 mL) in a dropwise fashion. The resulting dark red solution was stirred for 1 h at 0 °C. In a separate flask containing oxalyl chloride (1.16 mL, 13.5 mmol) in THF (22.5 mL) at -78 °C was added DMSO (1.92 mL, 27.1 mmol) over a period of 5 min. A solution of S-1 (2.11 g, 9.02 mmol) in THF (5 mL) was added, and the reaction mixture stirred for 15 min. Triethylamine (8.17 mL, 58.6 mmol) was then slowly added at -78 °C over a 15 min period and then the solution warmed to room temperature over 30 minutes. The reaction was diluted with 10 mL THF and filtered under suction. The residue was washed with two 10 mL portions of THF. The filtrate was concentrated to about 20 mL and cannulated into a 0 °C solution of the ylide generated above. The reaction mixture was warmed slowly to room temperature, stirred overnight, and then quenched with water. The aqueous layer was extracted three times with diethyl ether. The combined organic extracts were dried over Na_2SO_4 , filtered, concentrated *in vacuo*, and purified by silica gel column chromatography

(hexane:ethyl acetate = 10:1, slurry-packed with 1% Et₃N) to afford the bis-enol ether (1.29 g, 4.96 mmol) in a 55% yield as a 60:40 mixture of trans and cis isomers. ¹H NMR (CDCl₃, 300 MHz) δ 6.35 (d, *J*=12.6 Hz, 1.2H), 6.03 (d, *J*=6.3 Hz, 0.8H), 4.77 (tt, *J*=12.5, 7.6 Hz, 1.2H), 4.56-4.39 (m, 0.8H), 3.60 (s, 2.4H), 3.54 (s, 3.6H), 2.94-2.72 (m, 4H), 2.70 (dd, *J*=7.4, 1.5 Hz, 1.6H), 2.48 (dd, *J*=7.6, 7.6 Hz, 2.4H), 2.02-1.89 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 149.6, 148.4, 100.9, 96.8, 59.7, 56.1, 37.1, 36.6, 32.9, 32.2, 26.1, 25.5; IR (neat/NaCl) 2936, 2905, 2826, 1649, 1441, 1388, 1233, 1207, 1156, 1106, 935 cm⁻¹; ESI HRMS *m/z* (M+H)⁺ calcd 261.0977, obsd 261.0977.

