

Sunlight, Electrochemistry, and Sustainable Oxidation Reactions

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Supporting Information

1. General Methods

NMR spectra were acquired on a [Varian Mercury 300] spectrometer. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Flash column chromatography was performed using silica gel purchased from Sorbent Technologies. Enantiomeric excess was determined by HPLC on a Shimadzu LC-10AT. Thin layer chromatography was performed on Analtec UNIPLATE™ and visualized by ultraviolet irradiation, ceric ammonium molybdate, 2,4-dinitrophenylhydrazine or phosphomolybdic acid. Starting materials and reagents were purchased from Sigma-Aldrich.

Electrolysis reactions were run using a photovoltaic cell and light source (direct sunlight or hydroponic full spectrum 60 W 5500K compact fluorescent bulb) with an ammeter and optional coulometer connected in series. Output voltage of the photovoltaic cells varied from 6V – 35V depending on the light intensity, which was varied to control the current output. For reactions requiring higher current, a Topray Solar panel briefcase was connected in series as shown below. Alternatively, several 6V SolarMade photovoltaic cells can be connected in series to generate the equivalent amount of current. Reactions were carried out with a carbon cathode and reticulated vitreous carbon anode with vigorous stirring, unless mentioned otherwise.



2. Procedure for OsO₄ oxidation

A three-neck round bottom flask equipped with the RVC-anode and carbon-cathode was charged with substrate (104mg, 1.0 mmol), K₃Fe(CN)₆ (33 mg, 0.1 mmol), K₂CO₃ (420 mg, 3.0 mmol), (DHQD)₂PHAL (9mg, 0.01 mmol), and catalytic K₂OsO₂(OH)₄ (0.002 mmol) in 10 mL of 1:1 *t*BuOH:H₂O solvent. Once the desired charge, 2.5 F/mol, was passed through the flask at a current of roughly 2.5 mA , excess Na₂SO₃ (237 mg, 1.5 mmol) was added to the reaction

mixture and stirred for 30 minutes. The reaction was then poured into a separatory funnel, diluted with water, and then extracted with ethyl acetate. The combined organic layers were then dried over MgSO_4 , concentrated *in vacuo*, and then flash chromatographed (2:1 EtOAc:hexanes) through silica gel in order to afford 92% of the desired product in 94% e.e. The enantiomeric excess was determined by HPLC (Diacel, ChiraCel OD-H) with mobile phase 95:5 hexane:isopropanol, flow rate 1.0 mL min^{-1} , and detection at 204 nm. The spectral data matched the literature values.

3. Procedure for RuO_4 oxidation

A three-neck round bottom flask equipped with the RVC-anode and carbon-cathode was charged with 4-tert-butylcyclohexanol (156 mg, 1.0 mmol) and $\text{RuO}_2 \cdot \text{XH}_2\text{O}$ (3.7 mg, 0.02 mmol) in 5 mL of CCl_4 and 10 mL of a sat NaCl (aq) solution buffered to pH=4 with 0.2M NaH_2PO_4 . A constant current of roughly 20 mA (current direction switched every 1-2 min) was used to pass 4 F/mol of charge through the cell. The reaction mixture was then quenched with 0.5 mL of 2-propanol. The reaction was poured into a separatory funnel, diluted with water, and then the aqueous phase extracted with dichloromethane. The combined organic layers were dried over MgSO_4 , concentrated *in vacuo*, and then flash chromatographed (6:1 hexanes:EtOAc) through silica gel to afford an 82% of the desired product. The spectral data matched the data given in the literature.

4. Procedure for Heck oxidation

The anodic chamber of a standard H-cell under argon atmosphere was charged with 3-methylacetanilide (328mg, 2.2 mmol), n-butyl acrylate (409 μL , 2.8 mmol), hydroquinone (24 mg, 0.1 mmol), $\text{Pd}(\text{OAc})_2$ (49 mg, 0.1 mmol), and electrolyte tetrabutylammonium tetrafluoroborate (0.3M) in 15 mL of acetic acid. The cathodic chamber was charged with electrolyte (0.3 M) in 15 mL of acetic acid. The divided cell was fitted with a Pt foil anode and carbon cathode and then sonicated for 20 minutes. A constant current of roughly 1-3 mA was passed through the cell until 2.2 F/mol of charge was consumed. The contents of the anodic chamber were then poured into a separatory funnel, diluted with water, extracted with diethyl ether, and washed with saturated aqueous NaHCO_3 and brine solutions. The combined organic layers were dried over MgSO_4 , concentrated *in vacuo*, and flash chromatographed (4:1 heptane:EtOAc) through silica gel to afford 68% of the desired product. The spectral data matched the data given in the literature.

5. Procedure for Wacker oxidation

The anodic chamber of a standard H-cell under argon atmosphere was charged with 1-decene (190 μL , 1.0 mmol), electrolyte tetraethylammonium *p*-toluenesulfonate (0.5 M), tris(4-bromophenyl)amine (96 mg, 0.20 mmol), and $\text{Pd}(\text{OAc})_2$ (4mg, 0.05 mmol) in 24 mL of 9:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$. The cathodic chamber was charged with electrolyte (0.5 M) in an equivalent amount of solvent. The divided cell was fitted with two Pt foil electrodes and then sonicated for

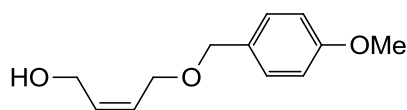
30 minutes. A constant current of roughly 8 mA was passed through the cell until 2.5 F/mol of charge was consumed. The contents of the anodic chamber were then poured into a separatory funnel, diluted with water, and then extracted with ethyl acetate. The combined organic portion was dried with MgSO₄, concentrated down *in vacuo*, and then flash chromatographed (5:1 hexanes:diethyl ether) through silica gel to afford 81% of the desired product. The spectral data matched the data given in the literature.

6. Procedure for TEMPO oxidation

A small vial sealed with a two-holed rubber stopper was fitted with the RVC-anode and carbon-cathode and then charged with methyl- α -D-glucopyranoside (97 mg, 0.5 mmol) and TEMPO (16 mg, 0.1 mmol) in 5 mL of a 0.4M Na₂CO₃/0.3M NaHCO₃ (aq) buffer solution. Roughly 30 mA of current was passed through the cell until 5.5 F/mol of charge was consumed. The reaction mixture was then poured into a separatory funnel, diluted with water, and then extracted with ethyl acetate in order to remove the TEMPO. To the aqueous portion following extraction was added 10 mL of Amberlite IR 120. The mixture was stirred for 2 hours, filtered, and concentrated *in vacuo*. An approximate yield of the desired carboxylic acid (98%) was determined by proton NMR with coumarin as the internal standard. The spectral data for the acid product matched the data provided in the literature.

7. Procedure for CAN oxidation

The anodic chamber of a standard H-cell under argon atmosphere was charged with (Z)-4-((4-methoxybenzyl)oxy)but-2-en-1-ol (34 mg, 0.16 mmol), electrolyte tetraethylammonium hexafluorophosphate (0.2 M), and ceric ammonium nitrate (9 mg, 0.1 mmol) in 6 mL 5:1 CH₃CN:H₂O. The cathodic chamber was charged with electrolyte (0.2 M) in an equivalent amount of solvent. The cell was fitted with a RVC anode and carbon cathode. Once the desired charge, 2.5 F/mol, was passed at roughly 2 mA, the contents of the anodic chamber were diluted with water, extracted with EtOAc, dried with MgSO₄, and concentrated *in vacuo*. Approximate yields of the desired products (88%) were determined by NMR with coumarin as the internal standard. The spectral data obtained matched the literature values.



(Z)-4-((4-methoxybenzyl)oxy)but-2-en-1-ol

Prepared from literature procedure, 43% yield (Chavan, S. P. and Harale, K. R. *Tet. Lett.* **2012**, 53 (35), 4683-4686.)

8. Procedure for (R,R)-Jacobsen's epoxidation

A three-necked round bottom flask equipped with the RVC-anode and carbon-cathode was charged with a solution of cis- β -methylstyrene (118 mg, 1.0 mmol) and (R,R)-(-)-N,N'-Bis(3,5-

di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride (33 mg, 0.05 mmol) in 5 mL of dichloromethane and 15 mL of an aqueous 1M NaCl solution. A constant current of roughly 16-17mA was passed through the flask until 7.5 F/mol of charge was consumed. At that point, the reaction was diluted with saturated aqueous NH₄Cl and the resulting mixture extracted with EtOAc. The combined organic layers were dried with MgSO₄ and concentrated *in vacuo*. Approximate yields for the 1*R*,2*S*-methylstyrene oxide (47-71%, 87% e.e.) and trans-methylstyrene oxide (9-11%) were determined by NMR with coumarin as the internal standard. The enantiomeric excess was determined using HPLC (Daicel, ChiralCel OD-H) with mobile phase 99:1 hexane:isopropanol, flow rate 1.0 mL min⁻¹, and detection at 254 nm. The spectral data obtained for the product matched the literature.