

Supporting Information
For
H₂-Driven Deoxygenation of Epoxides and Diols to Alkenes Catalyzed by
Methyltrioxorhenium (MTO)

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Experimental Methods

General. Methyltrioxorhenium (MTO) was purchased from Strem Chemicals, Inc. (Newburyport, MA). All other chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. Deoxygenation reactions were performed in a 100 mL, model number 4593, high-pressure Parr reactor, inside a fitted glass sleeve. Gas chromatography was performed with an Agilent Technologies 6890N Network GC System with a J&W Scientific DB-5 capillary column. Oven temperature was ramped from 40 to 70 °C at 5°C/min, and from 70 to 230 °C at 25°C/min in constant flow mode at 1.0 mL/min. Peaks in the GC trace were identified and quantified by comparison to an anthracene internal standard. Mass spectrometry was performed by the Purdue University Campus-Wide Mass Spectrometry Center on a Hewlett Packard Engine mass spectrometer (GC/MS).

Typical deoxygenation procedure. MTO (0.12 or 0.06 mmol) and epoxide/diol (1.2 mmol) were mixed together in 15 mL of THF and placed in a high-pressure Parr reactor. The inert atmosphere was replaced by H₂ and the reaction mixture was stirred under the desired pressure (80, 300, or 500 psi) of H₂. The heating mantle was programmed to ramp up at 60 °C/hour to 150 °C. Once at 150°C, the heating mantle was programmed to soak for the desired time (typically 8 h). After the soaking period, the reaction mixture was allowed to cool to room temperature. The entire sample was spiked with a known amount of anthracene (standard) and analyzed by GC. Product yields were calculated from GC-peak integrations versus anthracene and utilizing response factors that were obtained using authentic samples. All GC peaks were confirmed by GC/MS.

Liquid sampling procedure. MTO (8.0 mM) and styrene oxide (80 mM) were mixed together in 45 mL of THF in a high-pressure Parr reactor. The mixture was pressurized under dihydrogen (H₂) to 300 psi, heated to 150 °C and stirred. Liquid samples were retrieved from a side-arm attached to an internal sampling tube. Liquid samples were ca. 1.0 mL in size. These samples were spiked with a known amount of anthracene and analyzed by GC using response factors determined from authentic samples (of styrene oxide, phenyl-1,2-ethanediol, styrene, and ethyl benzene).

While the described sampling provides useful mechanistic information, it presents several difficulties and limitations. The larger volume of solvent makes stirring (and therefore H₂ phase transfer) less efficient. In addition, each time a sample is removed there is an increase in headspace, thereby decreasing the H₂ pressure. This decreases solution concentrations of H₂ and thus affects reaction rates. While the sampling experiments exhibit kinetic differences from small scale constant volume and pressure runs, they do provide useful qualitative information.