

# Oxidative Coupling of Thiols by Manganese Carbonyl Complexes

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## Introduction

The vital roles of organosulfur compounds in chemistry and biology,<sup>1</sup> and their transformations have always been of interest, in particular the oxidation of thiols into disulfides. However, such reactions often need a basic catalyst, or stoichiometric amounts of oxidants (e.g. sulfoxides, and halogens),<sup>2</sup> which commonly generate unwanted side-products. In addition, many of such protocols require costly and toxic reagents and/or long reaction times. Their syntheses sometimes suffers from over-oxidation, producing sulfoxides, sulfones, thiosulfinates, and thiosulfonates.<sup>9</sup>

In this work, we investigate a greener catalytic system: the photo-catalyzed conversion of thiols into disulfides using organometallic manganese complexes:  $\text{CpMn}(\text{CO})_3$  and  $\text{Mn}(\text{CO})_5\text{Br}$ , with dihydrogen as the only side-product. Interestingly, the manganese systems exhibit good chemoselectivity as the catalysis is efficient even in the presence of numerous functional groups. Their mechanisms have also been investigated via FTIR and NMR spectroscopy.

## Experimental

All reactions and manipulations were performed under vacuum using standard vacuum-line techniques for  $\text{CpMn}(\text{CO})_3$ , and under atmospheric conditions for  $\text{Mn}(\text{CO})_5\text{Br}$ . The metal complex and the respective thiol were added into a round-bottom flask which contained 0.5 cm<sup>3</sup> of solvent. The solutions were laser irradiated (355 nm, ~13 mJ/pulse), and stirred at room temperature for 2.5 h.

Photolysis experiments were performed using a Quanta-Ray PRO-series pulsed Nd:YAG laser (355 nm). Hydrogen gas was detected using a Balzer Prisma QMS 200 residual mass analyzer. IR spectra were recorded with a Shimadzu IR Prestige-21 Fourier-Transform IR spectrometer (1000–4000 cm<sup>-1</sup>, 1 cm<sup>-1</sup> resolution, 8 scans co-added for spectral averaging) using a 0.05 mm pathlength calcium fluoride cell. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AV 500 Fourier-Transform spectrometer operating at ca. 500 MHz. The chemical shifts were reported relative to TMS. Mass spectra of the disulfide products were recorded with a Finnigan Mat 95XL-T spectrometer.

## Results/Discussion

355nm laser irradiation of the manganese complexes with the mono-functional thiols produced the corresponding disulfides in excellent yields, with dihydrogen as the only side-product. <sup>1</sup>H-NMR and EI-MS have been used to confirm the identities of the organic products. The isolated disulfide yields are in excellent agreement with our method of using NMR quantification.

Dihydrogen has been detected in quantitative yields relative to the disulfides using EI-MS (Figure 1), which allows us to propose that the transformation is indeed very clean. The absence of the other commonly encountered over-oxidation products, such as sulfones and sulfoxides serves as further support.

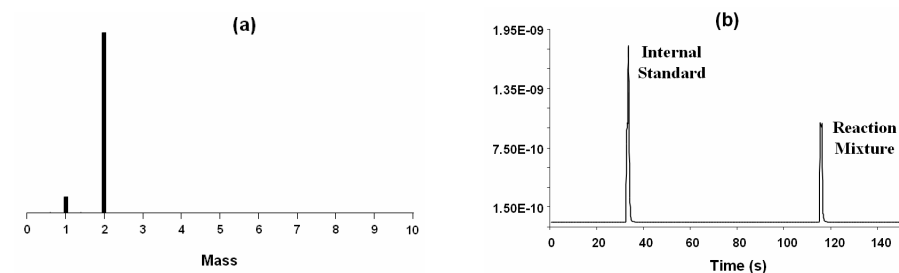


Figure 1. Photolysis of manganese carbonyl with hexadecanethiol in cyclohexane. a) Gas-phase mass spectrum indicating the formation of dihydrogen. b) Mass spectrum of dihydrogen (m/e value of 2) scanned overtime.

As the transformation involving mono-functional thiols to their respective disulfides has been shown to be efficient, we proceeded to investigate the one-pot irradiation in the presence of numerous functional groups. The system showed tolerance towards a wide variety of functional groups, such as alcohols, alkenes, alkynes, and esters as evidenced by unaffected disulfide yields. The presence of other functional groups such as ethers, ketones, nitriles, siloxanes and phosphines reduce the disulfide yields although the process is still catalytic.

## References.

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