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Chemoselective Methyltrioxorhenium(VII)-Catalyzed Sulfoxidations with Hydrogen Peroxide

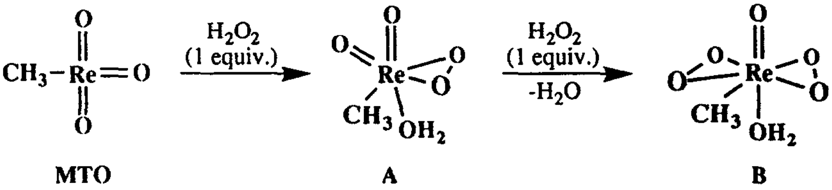
Waldemar Adam *, Catherine M. Mitchell, Chantu R. Saha-Möller

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

Abstract: The selective oxidation of sulfides to sulfoxides by hydrogen peroxide under methyltrioxorhenium(VII) catalysis was examined; a high selectivity of sulfoxide over sulfone was achieved, except in the presence of water, which enhanced sulfone formation.

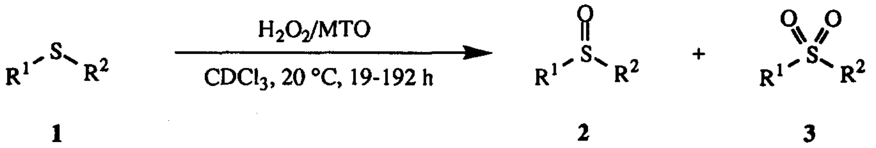
The selective oxidation of sulfides to sulfoxides has been of continued interest, for which numerous methods have been developed.1) Transition metal-catalyzed sulfoxidations have been reported for oxidants such as hydrogen peroxide,2) iodosobenzene,2b) iodylarenes,3) O_2/isobutyraldehyde,4) and ^tBuOOH.5) Furthermore, enzyme catalysis has been employed in a number of cases.6)

Methyltrioxorhenium (**MTO**) has been established as an efficient catalyst for the epoxidation and hydroxylation of olefins with hydrogen peroxide.7) **MTO** forms the mono- and diperoxo complexes **A** and **B** with H_2O_2 (Scheme 1), of which **B** has been structurally characterized by X-ray crystallography and proposed as the reactive oxygen-donating species for the epoxidation of alkenes on the basis of detailed mechanistic studies.7a) Oxidations of arenes to *para*-quinones8) and alkynes to α,β-unsaturated ketones or 1,2-diketones7b) and the Baeyer-Villiger rearrangement of ketones7b) can be performed catalytically by **MTO**. Recently it was reported that organophosphorus compounds, triphenylarsine, and triphenylstilbine can be catalytically oxidized with H_2O_2 by using **MTO** as catalyst.9) In addition, **MTO** has been used in the oxidation of a (thiolato)cobalt(III) complex by hydrogen peroxide.10) The versatility of this novel organometallic catalyst is manifested by the fact that olefin metathesis11) and the olefination of aldehydes with diazoalkanes12) have been accomplished. Surprisingly, to date no sulfoxidations have been documented for the MTO/H_2O_2 oxidant.



Scheme 1

As part of our broad-scope, metal-assisted oxidation program, we have subjected a selected set of sulfides to the catalytic oxidation by hydrogen peroxide with **MTO** as catalyst (Eq 1). The results are



(Eq 1)

	a	b	c	d	e
R^1	Me	^{t}Bu	Ph	Me	Me
R^2	Me	^{t}Bu	Ph	Bn	Ph

summarized in Table 1. In the presence of catalytic amounts of MTO (ca. 1 mol%), sulfides are oxidized by H_2O_2 smoothly and chemoselectively to sulfoxides in excellent yields. For instance, diphenyl sulfide (**1c**) gave almost exclusively the sulfoxide **2c** in 91% conversion (Entry 3). Similar results were obtained for benzyl methyl sulfide (**1d**), albeit in slightly lower conversion (Entry 4). Dimethyl sulfide (**1a**), as expected, was the most reactive substrate and substantial amounts of sulfone were obtained at complete conversion of the sulfide (Entry 1); however, presumably for steric reasons, the di-*tert.*-butyl sulfide (**1b**) gave only small

Table 1. MTO-catalyzed oxidation of sulfides **1** with H_2O_2 [a)]

Entry	R^1SR^2 (**1**)	H_2O_2 (equiv.)	MTO (equiv.)	Time (h)	Conv.[b)] (%)	Ratio [c)] R^1SOR^2 (**2**)	$R^1SO_2R^2$ (**3**)
1	**1a**	1.0	0.01	24	> 95	71	29
2	**1b**	1.0	0.01	24	73	97	3
3	**1c**	1.0	0.01	24	91	> 95	traces
4	**1d**	1.0	0.01	24	78	> 95	traces
5	**1d**	1.0	0.00	24	< 5	100	0
6	**1e**	1.0	0.01	24	83	97	3
7	**1e**	1.0	0.00	192	< 5	100	0
8	**1e**	2.0	0.04	19	> 95	32	68
9	**1e**	2.0	0.01	19	> 95	50	50
10	**1e**	1.0[d)]	0.01	24	72	82	18
11	**1e**	1.0	0.01	33	84	74	26

a) NMR scale reactions were carried out with 85% H_2O_2 in $CDCl_3$ at ca. 20 °C; D_2O was used as solvent for entry 11.

b) Mass balance > 95%.

c) Determined by ^1H NMR (250 MHz) analysis; error ca. ± 5% of the stated values; the ^1H NMR data of the sulfoxides **2** and sulfones **3** are in accordance with literature data.[1m), 13)]

d) 11% H_2O_2 was used.

quantities (3%) of sulfone at 73% conversion under otherwise identical oxidation conditions (Entry 2). A good yield and excellent selectivity for the sulfoxide were obtained for sulfide **1e** (Entry 6). Control experiments showed that an insignificant conversion of the sulfide occurred in the absence of **MTO** (Entries 5 and 7).

For more detailed investigations, thioanisole (**1e**) was chosen. Equimolar amounts of **1e** and aqueous 85% H_2O_2 with 1 mol% of the **MTO** catalyst gave the sulfoxide (**2e**) in high conversion (83%) of the sulfide and with excellent chemoselectivity (Entry 6). Larger amounts of the oxygen atom donor H_2O_2 and/or the catalyst (**MTO**) led to increased overoxidation to the sulfone **3e** (Entries 8 and 9). A comparison of Entries 6, 10, and 11 reveals that more overoxidation occurred with a larger content of water in the reaction mixture, in stark contrast to recent results in the photooxidation of disulfides.14) Possibly the enhanced electrophilicity of the sulfur atom in the sulfoxide due to hydrogen bonding with H_2O is responsible.

The **MTO**-catalyzed sulfoxidation with hydrogen peroxide offers a convenient and efficient method for the selective synthesis of sulfoxides. It should be of interest to apply such **MTO**-catalyzed sulfoxidations enantioselectively on prochiral sulfides with the help of optically active ligands.

EXPERIMENTAL

General: The ^1H NMR spectra were recorded on a Bruker AC 250 spectrometer.

General Procedure for the Sulfoxidation: To a solution of the catalyst MTO (0.002 - 0.005 mmol) in 0.6 ml $CDCl_3$ was added 85 % H_2O_2 (0.20 - 0.50 mmol). The resulting pale yellow emulsion was combined with the sulfide (0.20 - 0.50 mmol). The heterogeneous mixture was stirred at room temperature under an argon atmosphere for 19 - 192 h and the reaction mixture analyzed by ^1H NMR spectroscopy. The results are presented in Table 1.

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