Pergamon

Tetrahedron Letters 39 (1998) 7055–7058

TETRAHEDRON
LETTERS

Binuclear Manganese Complexes as Catalysts in the Selective and Efficient Oxidation of Sulfides to Sulfones

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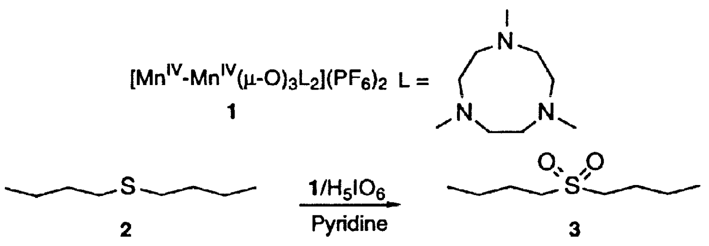
Received 1 June 1998; revised 13 July 1998; accepted 14 July 1998

Dedicated to the Memory of Sir Derek H. R. Barton

Abstract: The binuclear Mn^{IV}-Mn^{IV} manganese complex **1** catalyzes the periodic acid oxidation of sulfides to sulfones under mild conditions. The reaction was found to be highly selective giving almost quantitative yields of the sulfones even in the presence other easily oxidized groups. Only amines were found to hinder the reaction. © 1998 Elsevier Science Ltd. All rights reserved.

Due to the extensive use of sulfur derivatives in modern synthetic chemistry[1] the oxidation of sulfides to sulfones is well documented.[2] For this reason the search is still continuing for a reagent to carry out such transformations fast and efficiently.[3] Recently we reported the oxidation of selected organic substrates with periodic acid in the presence of binuclear manganese complexes.[4] Only phenols, certain dienes and sulfides were shown to react. The active oxidant in the reaction was believed to be a Mn^{V}=O-Mn^{IV} species which is formed from either Mn^{IV}-Mn^{IV} or Mn^{III}-Mn^{IV} binuclear complexes. Because of the low reactivity of the system towards olefins and alcohols, we envisaged the reagent to be selective in the oxidation of sulfides to sulfones in the presence of such functional groups. We now report the results of this study.

The catalyst studied was the binuclear complex **1**, $[Mn^{IV}\text{-}Mn^{IV}(\mu\text{-}O)_3L_2](PF_6)_2$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane) which was first reported by Wieghardt and Girerd[5a] and later by Hage [5b] as a catalyst for the epoxidation of olefins. Generally reactions (Table 1) were carried out in pyridine with ~1.8mol% of catalyst[6] even though the amount of catalyst could be reduced to 0.3mol% with little loss of reactivity (Entry 4). The oxidation of *n*-dibutyl sulfide **2** to *n*-dibutyl sulfone **3** was fast and efficient, although the rate was dependent upon the concentration of the solution (Entries 2 and 3). When **1** was omitted from the reaction only the sulfoxide was formed after 3.5h (Entry 1). During the reaction a precipitate forms which was shown to be a complex of iodic acid and pyridine and not the catalyst. The catalyst was shown to be robust as filtration of the precipitate and addition of fresh portions of the sulfide and periodic acid did not affect catatlytic oxidation. This was repeated ten times without any effect on the rate or yield of the reaction.[7]



Scheme 1

PII: S0040-4039(98)01518-4

Table 1: Catalytic oxidation of sulfides to sulfones with **1** and periodic acid.[a]

Entry	System Substrate (2mmol)	 H_5IO_6 (mmol)	Reaction Time (h)	Yield[b] (%) $R_1\text{-}S\text{-}R_2$	 $R_1\text{-}S(O)\text{-}R_2$	 $R_1\text{-}S(O_2)\text{-}R_2$
1[c]	**2**	4	3.5	3	96	trace
2[c]	2	4	0.5	trace	34	65
			1	0	4	94
			1.5	0	1	99 (95[f])
3[c,d]	2	4	0.5	41	55	2
			1	20	68	11
			1.5	8	52	39
4[c,e]	2	4	0.5	30	66	4
			1	3	30	67
			1.5	0	4	94
5[c]	**4**	4	2.5	15	28	55
			overnight	0	0	91
6[c]	**5**	4	20	0	0	96
7[c]	**6**	8	21	0	0	84
8[f]	**7**	4	overnight	-	-	84
9[f]	**8**	8	overnight	-	-	93
10[f]	**9**	4	overnight	-	-	91
11[f]	**10**	4	overnight	-	-	88
12[f]	**11**	4	overnight	-	-	89
13[f]	**12**	4	overnight	-	-	92
14[f, g]	**13**	4	overnight	-	-	85
15[f, g]	**14**	4	overnight	-	-	87
16[f,g]	**15**	4	overnight	-	-	91
17[f]	**16**	4	overnight	-	-	85
18[f,h]	**17**	7	3 days	-	-	86
19[f]	**18**	4	overnight	-	-	96
20[f,h]	**19**	7	3 days	-	-	0

a) Reactions were carried out with 30mg of **1** in pyridine (10ml) unless stated otherwise. b) Known compounds were identified by comparison with authentic samples. c) Yields of products were determined by GC analysis. d) 30ml of pyridine was used. e) 5mg of **1** was used. f). Yields stated are for isolated products. g) Sulfones from **13**, **14** and **15** are new compounds and gave satisfactory HRMS or elemental analysis. h) 3.5mmol of substrate was used.

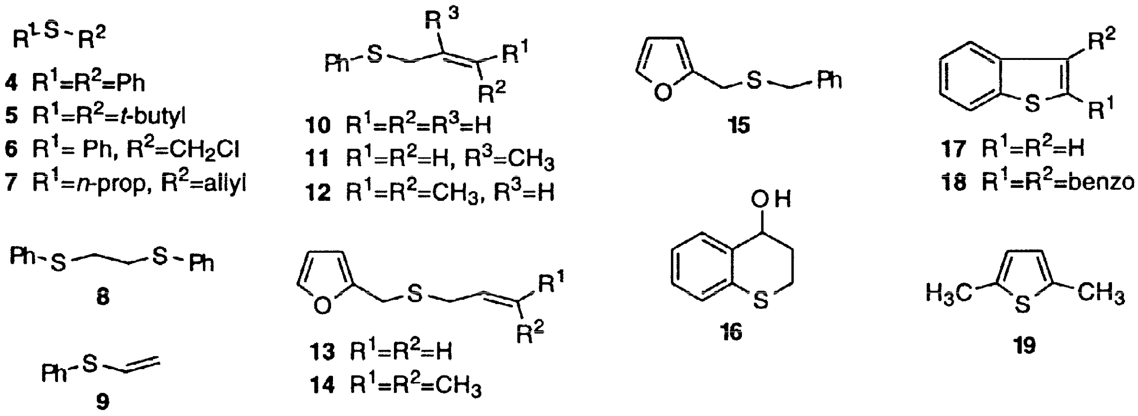
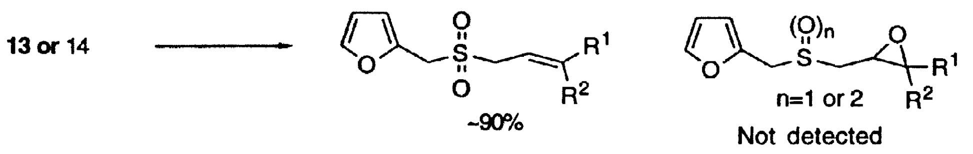


Figure 1

Aryl sulfides and hindered sulfides were also converted smoothly to the corresponding sulfones although the reaction times were longer. The selectivity of the system was indicated by the conversion of phenyl vinyl sulfide to phenyl vinyl sulfone without the formation of any other oxidation products (Entry 10). The same was observed with the phenyl allyl sulfides, **9-11**, and also for the furan derivatives **13-15** which gave only the sulfones in high yields with no oxidation on the heterocycle, olefin or benzyl position (Scheme 2).



Scheme 2

The value of the reagent system was fully demonstrated when thiochroman-4-ol **16** was converted to thiochroman-4-ol S,S-dioxide in 85% isolated yield. The benzyl portion is reported to be readily oxidized with *o*-iodoxybenzoic acid.[8] Hage and Feringa[9] also reported that **1** and hydrogen peroxide converts benzyl alcohol to benzaldehyde and benzoic acid which is not observed under our conditions. We found only one previous example where the sulfide was oxidized directly to the sulfone. Rozen[3] recently oxidized **16** without affecting the alcohol by reaction with HOF•CH_3CN complex. Although benzothiophene and dibenzothiophene (Entries 18 &19) reacted slowly, the yields were still high. The less reactive 2,5-dimethylthiophene (Entry 20) failed to give any product under these conditions.

Table 2: Competitive Oxidation of Dibutyl Sulfide in the Presence of Olefins, Alcohols and Amines

Entry	System[a] Substrate (mmol)	Yield[b] of S/SO/SO_2 BuSBu	BuSOBu	$BuSO_2Bu$
1	*n*-Dibutyl sulfide (2)	0	1	99
2	*n*-Dibutyl sulfide (2) Styrene (2)	0	1	99
3	*n*-Dibutyl sulfide (2) Linoleic acid (1)	0	1	99
4	*n*-Dibutyl sulfide (2) Ethyl linoleate (1)	0	1	99
5	*n*-Dibutyl sulfide (2) cycloheptatriene (1)	1	12	87
6	*n*-Dibutyl sulfide (2) Benzyl alcohol (2)	0	3	95
7	*n*-Dibutyl sulfide (2) N,N-Diethylaniline (2)	77	19	2
8	*n*-Dibutyl sulfide (2) Triethylamine (2)	25	44	29

a). Reactions were carried out in pyridine (10ml) with a catalytic amount of **1** (30mg). b) Yields of sulfides, sulfoxides and sulfones were determined by GC analysis of the crude reaction mixture.

The selectivity of the reagent towards sulfides was reaffirmed by competition reactions between *n*-dibutyl sulfide with styrene, linoleic acid, ethyl linoleate, cycloheptatriene and benzyl alcohol (Table 2). In all the above experiments only the sulfone was formed with no oxidation of the other substrate (Entries 2-6). The only functional group which was not compatible with the oxidation was the amine function. When the oxidation was carried out in the presence of N,N-diethylaniline or triethylamine the yield of the sulfone was dramatically reduced (Entries 7 and 8). Pyridine, the solvent of the reaction, does not react as no N-oxide could be detected even after 24h.

In conclusion we have demonstrated that **1**/periodic acid in pyridine is a fast and efficient system for the conversion of sulfides to sulfones. The system has also been shown to be highly selective towards sulfide oxidation even in the presence of other readily oxidized groups with the exception of amines

ACKNOWLEDGMENTS

We thank Unilever, the Welch Foundation and the Schering-Plough Corporation for the support of this work and Dr. Ronald Hage for his comments and for generous gifts of manganese complexes (Unilever).

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6. Typical reaction conditions for sulfide oxidation: *n*-Dibutyl sulfide (2mmol) was dissolved in pyridine (10ml) at room temperature. The catalyst **1** was added (30mg, ~1.8mol%) followed by periodic acid (4mmol) and the reaction mixture stirred rapidly. A complex of iodic acid/ pyridine slowly forms as the reaction progresses. Reaction times and product distribution were monitored by GC analysis for volatile compounds. Yields for other derivatives were detemined by isolation of the product.
7. Turnover numbers for the catalyst were ~600.
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