Asymmetric Oxidation of Sulfides with Molecular Oxygen Catalyzed by β-Oxo Aldiminato Manganese(III) Complexes

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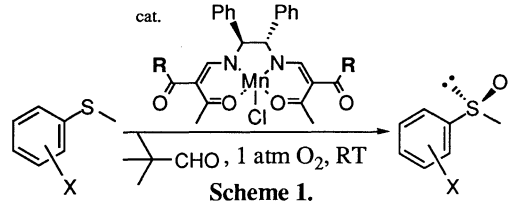
Enantioselective aerobic oxidation of sulfides with combined use of molecular oxygen and pivalaldehyde afforded the optically active sulfoxides using β-oxo aldiminato manganese(III) complex catalysts. For example, 2-chlorophenyl methyl sulfide afforded optically active sulfoxide in 72% enantiomeric excess.

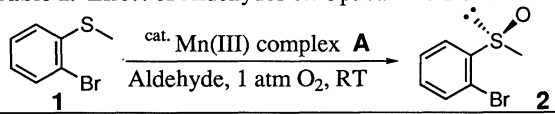
Utilization of molecular oxygen, one of the most useful oxidants, is quite an attractive topic in our research work. Recently, we have reported a novel method for the preparation of optically active epoxides from the corresponding unfunctionalized olefins catalyzed by optically active manganese(III) complexes with combined use of molecular oxygen and pivalaldehyde.[1-3] Then, oxidation of sulfides forming the corresponding optically active sulfoxides was tried in order to expand the scope of substrates to which the aerobic asymmetric oxidation can be applied. Optically active sulfoxides are important compound to build new chiral centers in organic synthesis,[4] and much effort has been made to develop the methodology for preparation of optically active sulfoxides.[5] In these days, the direct asymmetric oxidation of sulfides has drawn special attention, and some interesting results using hydroperoxide,[6] *N*-sulfonyloxaziridine,[7] iodosylbenzene,[8,9] or hydrogen peroxide[10] as oxidant have been reported, although there are still few examples on the utilization of molecular oxygen. In this communication, we would like to report the aerobic asymmetric oxidation of sulfides by using optically active β-oxo aldiminato manganese(III) complex catalysts in the coexistence of aldehyde.

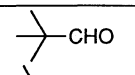
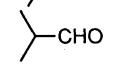
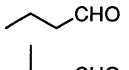
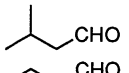
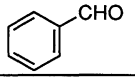


Scheme 1.

At first, several aldehydes were screened by taking the oxidation of 2-bromophenyl methyl sulfide (**1**) catalyzed by optically active Mn(III) complex **A** as a model reaction. When pivalaldehyde was employed, the corresponding sulfoxide **2** was obtained in 52 %ee (Entry 1 in Table 1), while the optical yields of the sulfoxide were less than 46 %ee in cases of use of isobutyraldehyde, butyraldehyde, and isovaleraldehyde (Entries 2, 3, and 4). It was found that aldehyde with a bulky alkyl group such as *tert*-butyl group, was effective in improving the optical yield of sulfoxide. This result suggested that aldehyde moiety was involved in reactive intermediate in the present aerobic oxidation.[2] The sulfide **1** was hardly oxidized when benzaldehyde was used as a reductant (Entry 5). Pivalaldehyde was also most effective with respect to chemical yield (73% yield, Entry 1).

Table 1. Effect of Aldehydes on Optical Yield of Sulfoxide



Entry[a]	Aldehyde	Yield / %	Optical yield / %ee[b]
1		73	52
2		39	46
3		38	42
4		23	44
5		trace	—

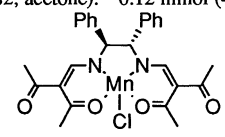
[a]Reaction conditions; sulfide 0.25 mmol, aldehyde 0.75 mmol, Mn(III) complex **A** (**R**=Me in Scheme 1) 0.03 mmol (12 mol%) in toluene 2 ml, RT, 1 atm O_2. [b]Determined by HPLC analysis (Daicel Chiralcel OB).

In both cases of using (*S,S*)-β-oxo aldiminato Mn(III) complex **A** and (*S,S*)-salen Mn(III) complex **B** as catalysts, the obtained sulfoxide **2** had the same absolute configuration (Entries 1 and 2 in Table 2). The present enantioselection by using (*S,S*)-Mn(III)-complex catalyst gave the opposite absolute configuration to that obtained when terminal oxidant such as iodosylbenzene[9] or hydrogen peroxide[10] was used. Furthermore, the absolute configuration of the sulfoxide **2** was reversed by adding a catalytic amount of *N*-methylimidazole in the above oxidation (Entry 3). The similar results were observed in case of the aerobic asymmetric epoxidation of unfunctionalized olefins.[3] Then, it was indicated that acylperoxo-Mn complex behaved as the reactive intermediate in the absence of *N*-methylimidazole, and oxo-Mn complex by adding *N*-methylimidazole, respectively,

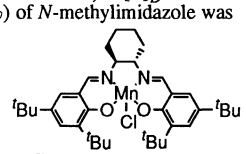
Table 2. Suitable Mn(III) Complex for Aerobic Asymmetric Oxidation of Sulfide

Entry[a]	Complex	Yield / %	Optical yield / %ee[b]
1	**A**	73	52 (-)[c]
2	**B**	54	18 (-)
3[d]	**B**	71	25 (+)

[a]Reaction conditions; sulfide **1** 0.25 mmol, pivalaldehyde 0.75 mmol, Mn(III) complex 0.03 mmol (12 mol%) in toluene 2 ml, RT, 1 atm O_2. [b]Determined by HPLC analysis (Daicel Chiralcel OB). [c]$[\alpha]_D^{30}$ -130° (*c* 0.182, acetone). [d]0.12 mmol (48 mol%) of *N*-methylimidazole was added.

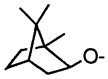
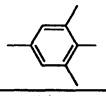


A (*S,S*)-β-Oxo aldiminato Mn(III)



B (*S,S*)-Salen Mn(III)

Table 3. Aerobic Asymmetric Oxidation of Sulfide Catalyzed by β-Oxo Aldiminato Mn(III) Complexes

Entry[a]	R		Yield / %	Optical yield / %ee[b]
1	Me-	C	73	52
2	EtO-	D	95	60
3		E	88	60
4		F	94	62
5		G	91	66

[a]Reaction conditions; sulfide **1** 0.25 mmol, pivalaldehyde 0.75 mmol, Mn(III) complex 0.03 mmol (12 mol%) in toluene 2 ml, RT, 1 atm O_2. [b]Determined by HPLC analysis (Daicel Chiralcel OB).

in the oxidation of sulfide. Judging from the results of optical yields in Table 2, β-oxo aldiminato Mn(III) complex catalyst was more effective than salen Mn(III) complex catalyst in the present aerobic asymmetric oxidation of sulfide.

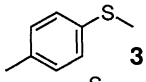
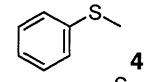
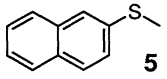
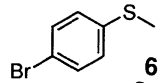
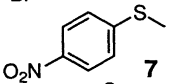
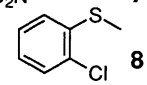
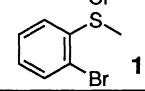
Next, the substituent group (**R** in scheme 1) in the β-oxo aldiminato ligand was modified to improve optical yield of the sulfoxide **2**. It was shown that the complex containing bulkier substituent group had effects on the enantioselection in the present oxidation (Table 3). In case of using β-oxo aldiminato Mn(III) complex **G** as the catalyst, the corresponding sulfoxide was obtained in 66 %ee (Entry 5).

The present system was applied to the aerobic asymmetric oxidation of various sulfides[11] (Table 4). In case of 2-chlorophenyl methyl sulfide (**8**), the sulfoxide was obtained in 72 %ee (Entry 6). The optical yield of the sulfoxide derived from 2-bromophenyl methyl sulfide (**1**) is superior to that of the sulfoxide derived from 4-bromophenyl methyl sulfide (**6**), suggesting that *o*-position was preferable to *p*-position in improving optical yield (70 %ee and 61 %ee, respectively, Entries 4 and 7).

A typical procedure is described for the oxidation of 2-chlorophenyl methyl sulfide (**8**, Entry 6 in Table 4); to a mixture of (*S*,*S*)-β-oxo aldiminato Mn(III) complex **G** (16.4 mg, 0.0225 mmol, 18 mol%) in *m*-xylene (4.0 ml) was added a solution of 2-chlorophenyl methyl sulfide (19.8 mg, 0.125 mmol) and pivalaldehyde (32.3 mg, 0.375 mmol) in *m*-xylene (1.0 ml), and stirred overnight at room temperature under an oxygen atmosphere. After the evaporation of solvent, crude product was purified by silica-gel column chromatography (hexane / ethyl acetate, 2 / 1) to afford the corresponding sulfoxide in 72% yield (15.8 mg). The enantiomeric excess was determined to be 72 %ee by HPLC analysis (Daicel Chiralsel OB).

It is noted that the various sulfides were oxidized into the corresponding optically active sulfoxides with combined use of molecular oxygen and pivalaldehyde using β-oxo aldiminato Mn(III) complex catalysts.

Table 4. Examples of Aerobic Asymmetric Oxidation of Sulfides

Entry[a]	Sulfide	Yield / %	Optical yield / %ee
1[b]	 **3**	58	44[c]
2[b]	 **4**	66	51[c]
3[b]	 **5**	57	51[d]
4[b]	 **6**	55	61[d]
5	 **7**	44(10)[e]	69[d]
6	 **8**	72	72[d]
7[b]	 **1**	93	70[d]

[a]Reaction conditions; sulfide 0.125 mmol, pivalaldehyde 0.375 mmol, Mn(III) complex **G** 0.0225 mmol (18 mol%) in *m*-xylene 5 ml, RT, 1 atm O_2. [b]Another portion of pivalaldehyde (0.375 mmol) was added during reaction. [c]Determined by HPLC analysis (Daicel Chiralcel OD). [d]Determined by HPLC analysis (Daicel Chiralcel OB). [e]Sulfone was also obtained.

References and Notes

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