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Asymmetric Oxidation of Sulfides Using (Salen)manganese(III) Complex as a Catalyst

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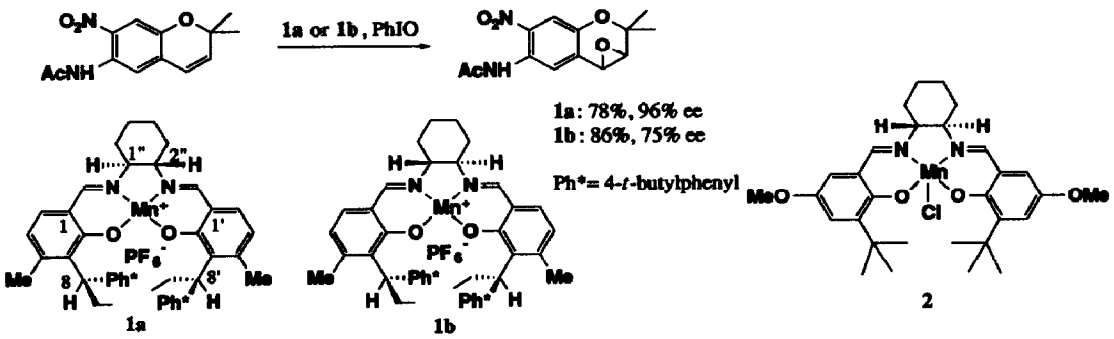
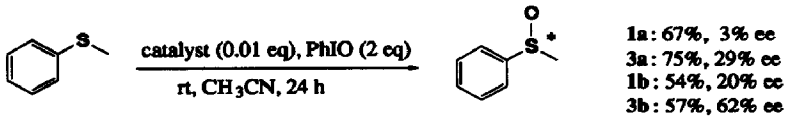
Abstract: Asymmetric oxidation of sulfides was examined by using (salen)manganese(III) complexes as catalysts and (8*S*,8'*S*,1"*S*,2"*S*)-complex (**3b**) was found to show high asymmetric induction up to 90% ee. To be interested, however, (8*R*,8'*R*,1"*S*,2"*S*)-complex (**1a**) that showed excellent asymmetric induction in the epoxidation of simple olefins was a poor catalyst for the oxidation of sulfides.

Asymmetric oxidation of sulfides is one of current topics and many useful methodologies for this purpose have been reported to date.[1,2,3] Some of these methodologies are well known to be also useful for the epoxidation of olefins. However, differing from epoxidation, there is no good methodology for catalytic asymmetric oxidation of sulfides, though some stoichiometric reactions show high enantioselectivity (>90% ee).[1,3b] Recently we found that optically active (salen)manganese(III) complexes having asymmetric carbons at C8, C8', C1", and C2" were efficient catalysts for asymmetric epoxidation of simple olefins (Scheme 1).[4] To extend the scope of this-type of salen catalyst and to develop an efficient methodology for catalytic asymmetric oxidation of sulfides, we examined oxidation of sulfides using these salen complexes as catalysts.[5]



Scheme 1

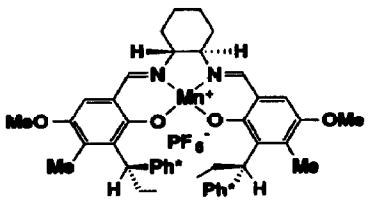
Since we had already found that (8*R*,8'*R*,1"*S*,2"*S*)-(salen)manganese(III) complexes such as **1a** showed higher asymmetric induction than diastereomeric (8*R*,8'*R*,1"*R*,2"*R*)-complexes such as **1b** in epoxidation (Scheme 1), we first examined the oxidation of methyl phenyl sulfide in the presence of various (8*R*,8'*R*,1"*S*,2"*S*)-complexes using iodosylbenzene as a terminal oxidant but all the complexes exhibited very poor asymmetric induction. For example, epoxidation of 6-acetamido-2,2-dimethyl-7-nitrochromene with **1a** proceeded with 96% ee but oxidation of methyl phenyl sulfide with the same catalyst showed only 3% ee (Scheme 2). However, chemical yield of the desired sulfoxide was good (67%) and the undesired sulfone was a minor product (30%). Although Jacobsen recommended to use hydrogen peroxide as a terminal oxidant to



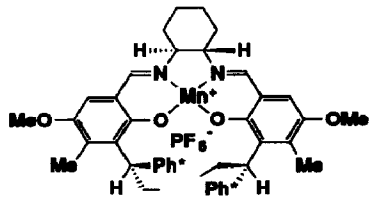
Scheme 2

prevent overoxidation to sulfone in the oxidation of sulfides using **2** as a catalyst,[5c] it was not a good terminal oxidant in our system. Use of hydrogen peroxide led to considerably lower chemical yield as compared with iodosylbenzene in all cases (cf. Table 1, entries 1 and 2). The origin of these differences between their and our reaction systems is unclear.

Recently Fujita et al. reported that (salen)vanadium complexes having an electron-donating group in its salicylaldehyde part showed better asymmetric induction than the corresponding salen complex having no such group.[5b,6] According to this paper, we also synthesized the salen complex **3a** having methoxy group at C5



3a



3b

and C5', and examined oxidation. However, asymmetric induction by **3a** was only moderate (29% ee, Scheme 2). After many trials for years, we incidentally found that the diastereomeric (8*R*,8'*R*,1"*R*,2"*R*)-**1b** showed much higher asymmetric induction than **1a**, though insufficient level (Scheme 2). With this result in hand, we further synthesized complex **3b** bearing methoxy group in the salicylaldehyde part and found that **3b** showed the remarkably enhanced asymmetric induction (62% ee) and that the ratio of sulfoxide to sulfone was also improved to 6.9:1. Since we had found that addition of donor ligand such as pyridine *N*-oxide to salen-catalyzed epoxidation system improved its enantioselectivity,[4a] we also examined oxidation of methyl phenyl sulfide in the presence of various donor ligands. However, all the ligands examined showed the negative effect on enantioselectivity, though the ratio of sulfoxide to sulfone was further improved to 47:1 when pyridine *N*-oxide was used. To explore the temperature effect on enantioselectivity, the reaction at -20 °C was next examined and slightly improved enantioselectivity (63% ee) was observed. The reaction at -20 °C also suppressed the formation of undesired sulfone (Table 1, entries 1 and 3). Accordingly, oxidation of various sulfides was examined at -20 °C. Sulfides bearing electron-withdrawing group such as bromo or nitro group in its aryl group showed higher enantioselectivity (entries 4-7) than sulfide bearing electron-donating group (entry 8), suggesting that the reaction proceeded via formation of charge transfer complex.[7] Oxidation of methyl *o*-nitrophenyl sulfide exhibited the highest enantioselectivity of 90% ee.

Recently we proposed that olefin approaches metal-oxo bond along metal-C2" nitrogen bond axis in salen-catalyzed epoxidation reaction (Fig. 1).[8] This proposal also leads to a reasonable explanation about the difference in stereochemistry of the epoxidation of simple olefins and of the oxidation of sulfides. In the case of epoxidation with **1a** as a catalyst, C8'-*t*-butylphenyl group interacts with the substituent of the oncoming olefin so that **1a** can discriminate olefin's enantioface (Fig. 1, C). In the case of sulfide oxidation with **3a** as a

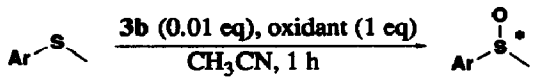
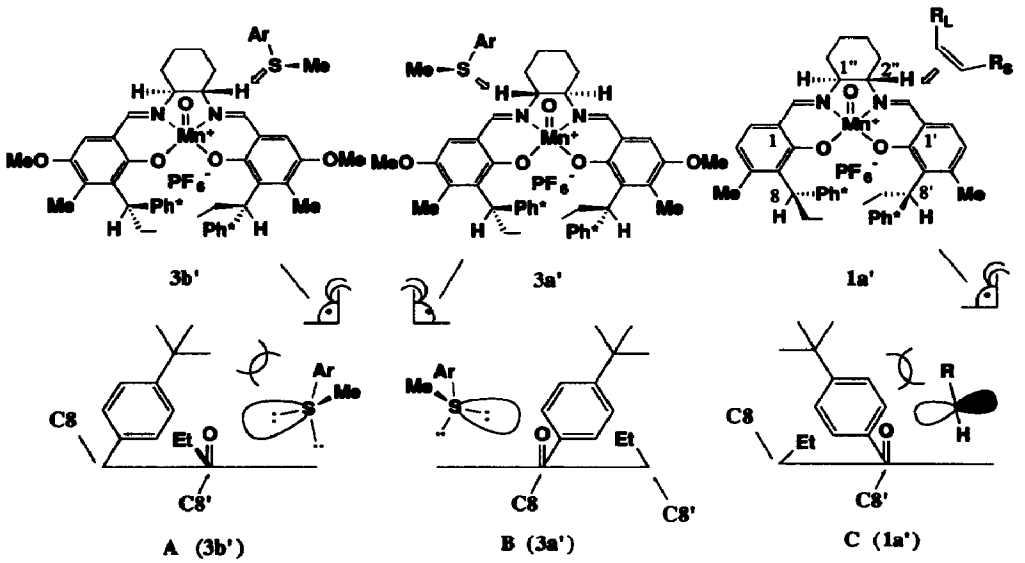


Table 1. Asymmetric oxidation of sulfides with (salen)manganese(III) complex as a catalyst

entry	substrate (Ar)	oxidant	Temp.	Yield (%)[a]		% ee	Abs. Confign.
1	Ph	PhIO	r.t.	57	(8)	62[b]	R[c]
2	Ph	H_2O_2	r.t.	9	(-)[d]	50[b]	R[c]
3	Ph	PhIO	-20 °C	76	(-)[d]	63[b]	R[c]
4	*o*-$NO_2C_6H_4$	PhIO	-20 °C	51	(-)[d]	90[e]	-
5	*p*-$NO_2C_6H_4$	PhIO	-20 °C	67	(5)	86[f]	-
6	*o*-BrC_6H_4	PhIO	-20 °C	74	(-)[d]	88[g]	-
7	*p*-BrC_6H_4	PhIO	-20 °C	63	(2)	75[g]	-
8	*p*-$MeOC_6H_4$	PhIO	-20 °C	45	(4)	40[e]	-

a) Isolated yield. The number in parentheses is the yield of the corresponding sulfone.
b) Determined by HPLC analysis (Daicel, chiralcel OD, hexane-*i*-PrOH 9:1).
c) Determined by comparison of optical rotation with reported value (reference 5b).
d) Formation of sulfone was not detected by TLC analysis.
e) Determined by HPLC analysis (Daicel, chiralcel OD, hexane-*i*-PrOH 30:1).
f) Determined by ^{1}H NMR (400 MHz) analysis using (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol as a shift reagent.
g) Determined by ^{1}H NMR (400 MHz) analysis using (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl as a shift reagent.



The views of oxo species (1a', 3a', and 3b') derived from 1a, 3a and 3b, from C3' or C3 substituent side

Fig. 1

catalyst, however, C8-*t*-butylphenyl group can not interact with the oncoming sulfide, because the sulfur atom takes sp^3-configuration and, therefore, substituents of the sulfide stay behind the sulfur atom. Accordingly, high enantioselective oxidation of sulfides by **3a** is difficult (**B**). On the other hand, C8-*t*-butylphenyl group in

3b is directed toward the oncoming sulfide and interacts with sulfide's substituent (A). This model correctly predicts the stereochemistry of methyl phenyl sulfoxide obtained with **3b** to be *R*.

Typical experimental procedure is exemplified by the oxidation of methyl *o*-nitrophenyl sulfide. Methyl *o*-nitrophenyl sulfide (16.9 mg, 0.1 mmol) was added to a solution of **3b** (1.0 mg, 1 μmol) in acetonitrile (1 ml) and the mixture was cooled to -20 °C. To this solution was added iodosylbenzene (22.0 mg, 0.1 mmol) at the same temperature and the whole mixture was stirred for 1 h, then allowed to warm to room temperature, and filtrated. The filtrate was concentrated and purified by thin layer chromatography on silica gel (hexane-ethyl acetate = 1:1) to give the corresponding sulfoxide (8.7 mg, 51%). The enantiomeric excess of the sulfoxide was determined to be 90% by HPLC analysis (Daicel, chiralcel OD, hexane-*i*-PrOH 30:1).

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REFERENCES AND NOTES

1. a) Davis, F.A.; Reddy, R.T.; Han, W.; Carroll, P.J. *J. Am. Chem. Soc.*, **1992**, *114*, 1428-1437. b) Kagan, H.B.; Dunach, E.; Pitchen, P.; Deshmulh, M.N. *ibid.*, **1984**, *106*, 8188-8193.
2. Recently several chiral porphyrin complexes have been used as catalyts for asymmetric oxidation of sulfides with modest selectivity. a) Groves, J.T.; Viski, P. *J. Org. Chem.*, **1990**, *55*, 3628-3634. b) Naruta, T.; Tani, F.; Maruyama, K. *Tetrahedron: Asymmetry*, **1991**, *2*, 533-542. c) Halterman, R.L.; Jan, S.T.; Nimmons, H.C. *Synlett*, **1991**, 791-792. d) Chiang, L.-c.; Konishi, K.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.*, **1992**, 254-256.
3. a) Komatsu, N.; Nishibayashi, Y.; Sugita, T.; Uemura, S. *Tetrahedron Lett.*, **1992**, *33*, 5391-5394. b) Quite recently, Uemura et al. reported formation of highly optically pure sulfoxides (up to 96% ee) by combination of enantioselective oxidation of sulfides and kinetic resolution of the resulting enantiomerically enriched sulfoxides: Komatsu, N.; Hashizumi, M.; Sugita, T.; Uemura, S. *J. Org. Chem.*, **1993**, *58*, 4529-4533.
4. a) Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron: Asymmetry*, **1991**, *2*, 481-494. b) Hosoya, N.; Irie, R.; Katsuki, T. *Synlett*, **1993**, 261-263.
5. Previous examples of salen-catalyzed asymmetric oxidation, see: a) Nakajima, K.; Kojima, M.; Fujita, J. *Chem. Lett.*, **1986**, 1483-1486. b) Sasaki, C.; Nakajima, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 1318-1324. c) Palucki, M.; Hanson, P.; Jacobsen, E.N. *Tetrahedron Lett.*, **1993**, *33*, 7111-7114.
6. Jacobsen et al. also reported that (salen)manganese(III) complexes bearing electron-donating group showed higher asymmetric induction than the complexes bearing no such functional group in the epoxidation of simple olefins: Jacobsen, E.N.; Zhang, W.; Guler, M.L. *J. Am. Chem. Soc.*, **1991**, *113*, 6703-6704.
7. Naruta et al. reported that chiral "twin coronet" ironporphyrin-catalyzed oxidation of aryl methyl sulfides proceeds through one electron transfer process wherein the electronic nature of aryl substituents affects enantioselectivity to only a small extent (reference 2b).
8. Hosoya, N.; Hatayama, A.; Yanai, K.; Fujii, H.; Irie, R.; Katsuki, T. *Synlett*, **1993**, 641-645.

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