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Asymmetric Aerobic Epoxidation of Unfunctionalized Olefins Catalyzed by Optically Active α-Alkoxycarbonyl-β-ketoiminato Manganese(III) Complexes

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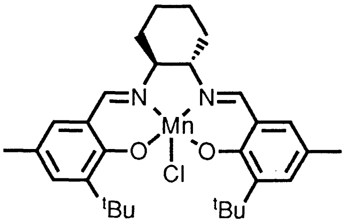
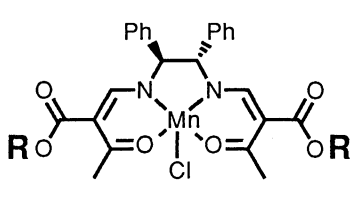
Optically active *N, N'*-ethylenebis(α-alkoxycarbonyl-β-ketoimine) was found to be a new class of effective ligand of manganese(III) complex catalyst for the asymmetric aerobic epoxidation of simple olefins, such as 1,2-dihydronaphthalene derivatives, to afford the corresponding optically active epoxides with good to high enantioselectivities.

β-Diketone derivatives are generally employed as one of the most basic ligands that form stable complexes with a wide variety of transition metals. Many kinds of 1,3-diketone derivatives have been used for the separation of metal ions in analytical chemistry or for the ligand of metal complex catalyst in organic synthesis.1) Various derivatives of β-diketone are easily prepared by common synthetic methods and are able to tune stereochemical or electrochemical properties, and it is possible, therefore, to control the chemical behavior of metal complexes, such as oxidation potentials. For example, it was reported from our laboratory that 1,3-diketone-type ligands having electron-withdrawing groups are quite effective for the cobalt(II) catalyst in "Oxidation-Reduction Hydration" of olefins with combined use of molecular oxygen and secondary alcohols,2) and 1,3-diketone-type ligands with electron-donating groups are favorable for nickel(II) complex catalyst in the aerobic epoxidation of olefins.3) In our previous communication, an asymmetric aerobic epoxidation of unfunctionalized olefins catalyzed by optically active manganese(III)-salen complexes (type **A**) with combined use of pivalaldehyde was described.4)

In this communication, we would like to report that optically active *N, N'*-1,2-diphenylethylenebis(α-alkoxycarbonyl-β-ketoimine)5) derived from β-dicarbonyl-type compound is a new class of effective ligand of manganese(III) complex catalyst (type **B**) for enantioselective aerobic epoxidation of simple olefins to give optically active epoxides with good to high enantioselectivities under an oxygen atmosphere with combined use of an aldehyde.



A



B

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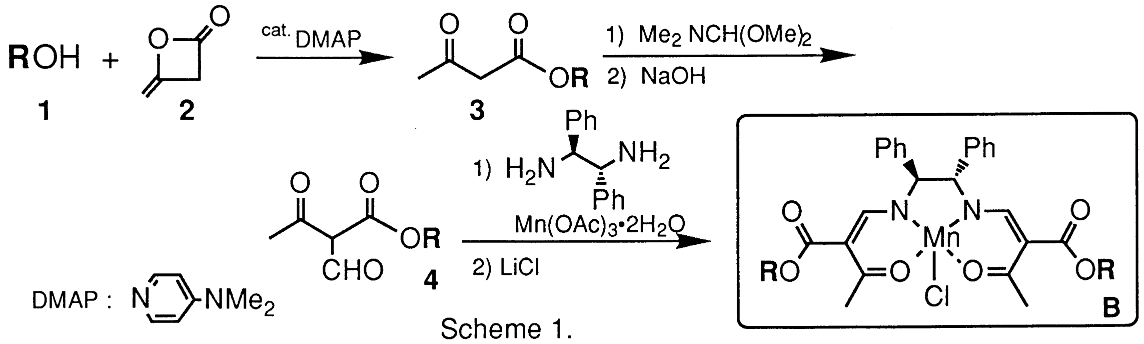
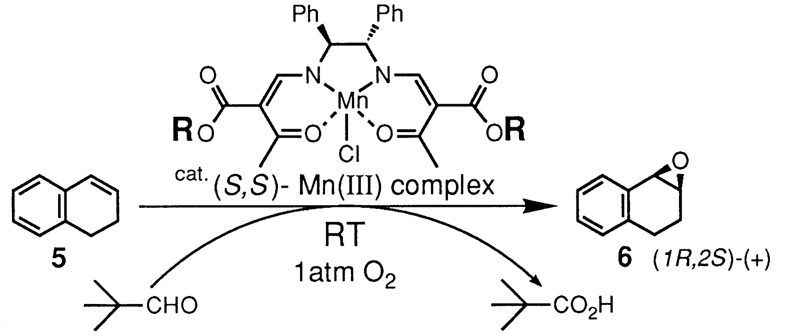
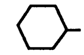
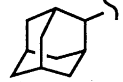
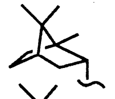
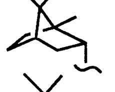


Scheme 1.

Synthesis of Mn(III) complexes **B** is shown in the above scheme. Alkyl acetoacetate **3** was prepared by the literature method,[6)] and treatment of **3** with dimethylformamide dimethylacetal[7)] and subsequent hydrolysis afforded aldehyde **4**. Formation of ketoimine-type ligand and complexation with Mn(III) was carried out by the template method,[8)] that is, a mixture of **4**, (*S*, *S*)-1,2-diphenylethylenediamine and Mn(III) acetate was heated at 80 °C in ethanol-dichloroethane solution followed by addition of lithium chloride.[9,10)] Manganese(III) complex (**B**) was isolated as dark brown powders after purification of a crude complex by column chromatography on silica-gel (acetone-dichloromethane) and reprecipitation (chloroform-ether).[11)]

Table 1. Asymmetric epoxidation of 1,2-dihydronaphthalene



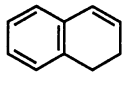
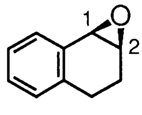
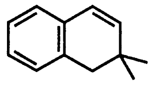
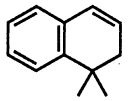
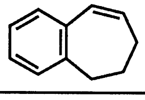
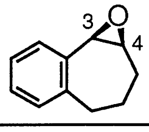
Entry[a)]	R		Yield / %[e)]	Optical yield / %ee[f)]
1	CH_3-	**B-1**	64	33
2	CH_3CH_2-	**B-2**	38	36
3		**B-3**	42	42
4		**B-4**	46	44
5[b)]		**(*R,R*)-B-5**	50	45[b)]
6[c)]		**(*S,S*)-B-5**	47	50
7[d)]		**B-6**	51	52

a)Reaction conditions; 1,2-dihydronaphthalene 0.8 mmol, pivalaldehyde 2.8 mmol, Mn(III) catalyst 0.104 mmol(13 mol%) in benzene 2 ml, RT, 1 atm O_2, 1 h. b) (*R,R*)-Diamine / (-)-borneol-catalyst was used, then the absolute configuration of the epoxide was (*1S,2R*)-(-). c) (*S,S*)-Diamine / (-)-borneol-catalyst was used. d) (*S,S*)-Diamine / DL-isoborneol-catalyst. e) Isolated yield. f) Determined by GC analysis (Chiraldex B-DA (20 m x 0.25 mm ID x 0.125 μ film), ASTEC Co.). Absolute configurations were (*1R,2S*)-(+) except Entry 5.

In the first place, steric effect of alkyl group in ester moiety in type-**B** Mn(III) complex upon optical yield was examined in the asymmetric epoxidation of 1,2-dihydronaphthalene with combined use of molecular oxygen and pivalaldehyde (Table 1). Epoxidation was carried out in benzene solution at room temperature and the optical yield was determined by GC analysis. As shown in Table 1, it was found that (*S, S*)-**B** catalyst derived from a bulkier alcohol is effective to improve the enantioselection in the present asymmetric epoxidation. Compared with the cases of using (*S, S*)-**B-1** (33% ee)[12] derived from methyl acetoacetate or (*S, S*)-**B-2** (36% ee) derived from ethyl ester, optically active epoxide **6** was obtained with better enantioselectivities by using Mn(III) complexes (*S, S*)-**B-3** and **B-4**, having bulkier substituents, such as cyclohexyl and adamantyl group (42% ee and 44% ee, respectively). When (*S, S*)-**B-5** and (*R, R*)-**B-5** derived from chiral (-)-borneol were used as catalysts, the absolute configurations and optical yields of epoxide **6** were (*1R, 2S*)-(+) (50% ee) and (*1S, 2R*)-(-) (45% ee), respectively (Entries 5 and 6).[13] These results suggest that enantioselection in the present asymmetric reaction could be controlled by optically active 1,2-diphenylethylenediamine and that contribution of chirality in ester moiety is not influential. Moreover, in the case of the Mn(III) complex **B-6** having bulky alcohol, DL-isoborneol, in ester moiety was used, optical yield was also improved up to 52% ee (Entry 7).

In every case, the absolute configuration of the obtained epoxide **6** was identified to be (*1R, 2S*) when (*S, S*)-complex **B** was used as a catalyst. It is interesting to point out here that the present asymmetric selection is a reversal of the reported results; for example, enantioselective epoxidations catalyzed by optically active Mn(III)-salen complex (type-**A**) by using iodosylbenzene as an oxidant (Jacobsen[14] and Katsuki[8]), or with combined use of molecular oxygen and an aldehyde in the presence of *N*-methylimidazole (Yamada[4]).

Table 2. Examples of asymmetric epoxidation

Entry[a)]	Olefin[b)]		Yield / %[c)]	Optical yield / %ee[d)]	Note
1		**5**	70	64	 (*1R,2S*)
2		**7**	40	53	
3		**8**	43	70	
4		**9**	52	84	 (*3R,4S*)

a)Reaction conditions; olefin 0.8 mmol, pivalaldehyde 2.8 mmol, Mn(III) catalyst (**B-6**) 0.104 mmol (13 mol%) in benzene 2 ml, 30 °C, 1 atm O_2, 1 h. b) Olefins were prepared from the corresponding tetralone derivatives. c) Isolated yield. d) Determined by GC analysis (Chiraldex B-DA).

Asymmetric aerobic epoxidation catalyzed by optically active manganese(III) complex **B-6** was successfully applied to several simple olefins, 1,2-dihydronaphthalene derivatives (Table 2). 1,2-Dihydronaphthalenes without any functional groups, **5**, **7**, and **8**, were converted into the corresponding epoxides with combined use of molecular oxygen and pivalaldehyde in good yields with good enantioselections, 64% ee, 53% ee, and 70% ee, respectively (Entries 1-3). In the case of enantioselective epoxidation of 6,7-dihydro-5*H*-benzocycloheptene (**9**), the optically active (*3R, 4S*)-(+)-epoxide was obtained with highly enantiomeric excess (84% ee, Entry 4).[15]

A typical procedure is described for the enantioselective epoxidation of 1,2-dihydronaphthalene (**5**, see Entry 1 in Table 2): To a solution of (*S, S*)-**B-6** (83 mg, 0.104 mmol) in benzene (1.0 ml) was added a solution of **5** (104 mg, 0.8 mmol) and pivalaldehyde (241 mg, 2.8 mmol) in benzene (1.0 ml), and the resulting solution was stirred at 30 °C$^{16)}$ for 1 h under an atmospheric pressure of oxygen. The crude product was poured into aqueous $NaHCO_3$ and extracted with ether. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. Purification by column chromatography on silica-gel (hexane-ethyl acetate) afforded the corresponding optically active epoxide, (*1R, 2S*)-(+)-1,2-epoxy-3,4-dihydronaphthalene(**6**), in 70% yield. The optical yield was determined to be 64% ee by GC analysis (Chiraldex B-DA, ASTEC Co.).

Further studies on the reactive intermediate and stereochemistry in the present reaction are under active investigation.

References

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10) The air oxidation of manganese(II) salt with the ligand prepared by aldehyde **4** and the optically active diamine afforded manganese(III) complex (**B**) in very low yield. See Ref. 9.

11) In the case of manganese(III) complex **B-6**, the chemical yields of each step were shown as follows; acetoacetate **3** (quantitative), aldehyde **4** (79%), manganese(III) complex **B-6** (25%).

12) By using Cyclo-**B-1** complex prepared from optically active (*S,S*)-1,2-diaminocyclohexane instead of (*S,S*)-1,2-diphenylethylenediamine, epoxide **6** was afforded in an optical yield of 9.3% ee (50% yield) under the same reaction conditions described in Table 1.

13) The absolute configuration of epoxide **6** was determined by comparing the sign of optical rotation with the reported value. D. R. Boyd, D. M. Jerina, and J. W. Daly, *J. Org. Chem.*, **35**, 3170 (1970).

14) W. Zhang, J. L. Loebach, S. R. Wilson, and E. N. Jacobsen, *J. Am. Chem. Soc.*, **112**, 2801 (1990).

15) For the absolute configuration of the epoxide derived from **9**, see Ref. 4.

16) The enantioselection in the present reaction was affected by temperature. In the present asymmetric epoxidation, reaction temperature between 25 °C (RT) and 30 °C is suitable for higher enantioselection.

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