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Aerobic Enantioselective Epoxidation of Styrene Analogues Induced by (β-Diketone)-iron(Ⅲ) Complex

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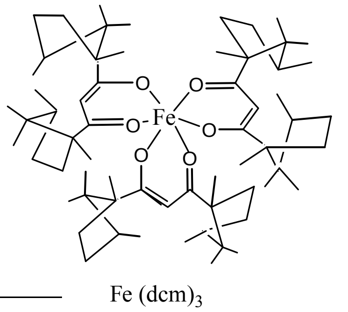
Abstract: Tris(d,d-dicampholylmethanato) iron（III）complex, Fe(dcm)$_3$, was found to be an excellent catalyst for asymmetric oxygenation of styrene analogues into the corresponding epoxides. Good chemical yields and higher enantioselectivity were obtained with combined use of molecular oxygen and an aldehyde at 30℃. Some factors influencing enantioselectivity were discussed.

Keywords: Epoxidation, oliefin, asymmetric catalysis, (β-diketone)-iron (III) complex.

Asymmetric oxidation is of general importance for the synthesis of optically active organic compounds. The enantioselective epoxidation of allyl alcohols, Sharpless and Katzuki introduced an extremely excellent translation metal-catalyzed oxygen transfer. The enantioselectivities of over 90 % are achieved[1]. Enantioselective epoxidation of unfunctionalized olefins, Jacobsen[2] and Katsuki[3] found that *cis*-disubstituted and trisubstituted olefins could be catalyzed by chiral (salen) manganese(III) complexes with high enantioselectivity. However, for asymmetric epoxidation of terminal olefins such as styrene, high enantioselectivity have not yet been devised[4]. Iron complexes are considered to be one of the most promising catalysts for oxygenation, because iron is a relatively inexpensive and less poisonous metal compared with other transition metals[5].

Scheme 1



Fe (dcm)$_3$

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Previously, we reported the asymmetric cyclopropanation[6~8] and cyclization of α-diazoketones[9] using a chiral complex Cu(dcm)$_2$ prepared from nature D-camphor and Cu(II) as catalyst, high enantioselectivities have been achieved.

In this work, we applied the chiral (β-diketone)-iron(III) complex, Fe(dcm)$_3$, that combined with chiral β-diketone Hdcm and Fe(III) as catalyst for the enantioselective oxidation of styrene analogues.

Results and Discussions

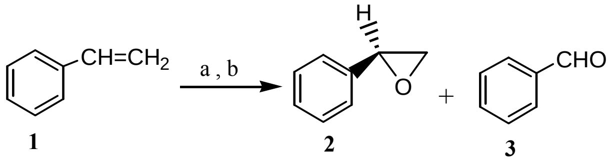
In order to examine the new catalyst Fe(dcm)$_3$, asymmetric epoxidation of styrene was performed. Styrene is highly reactive toward oxygenation and rather difficult to obtain styrene oxide due to cleavage of C=C bond in styrene into benzaldehyde. Thus, styrene was treated with combination of molecular oxygen and sacrificial aldehyde in the presence of a catalytic amount of Fe(dcm)$_3$.

Many aldehydes were tested and high *ee* value was obtained when the epoxidation was carried out with 2-ethylbutyraldehyde as sacrificial aldehyde(**Table 1)**.

A high chemical yield can be obtained at a higher temperature, as shown in **Table 2**. However, a lower *ee* value was obtained upon increasing the temperature. The preferable temperature range for this reaction is 20 or 30 ℃.

We then extended our investigation to some styrene analogues using 2 mol % of catalyst. The reaction of epoxidation was carried out at 30 ℃with 1,2-dichloroethane as the solvent, the results are summarized in **Table 3**. It was found that excellent enantioselectivities were obtained, when $R_1= R_2=$ H, $R_3= CH_3$ or Ph, while $R_1=R_3=$H, R_2

Scheme 2



a. Fe(dcm)$_3$; b. aldehyde + O$_2$

Table 1 The effect of aldehydes on the asymmetric epoxidation of styrene [a]

Entry	Aldehyde	Conversion (%)	Yield(%)		ee^b (%)	Config.[c]
			2	**3**		
1	propionaldehyde	89	31.3	51	56.8	S
2	*n*-butyraldehyde	93.4	55.6	36	58.7	S
3	*iso*-butyraldehyde	100	77.8	20	67.3	S
4	*n*-valeraldehyde	97.7	74.9	22	64.5	S
5	*iso*-valeraldehyde	100	80.6	14	73.4	S
6	2-ethylbutyraldehyde	100	89.7	7	78.1	S

a: Reactions were performed at 30℃ in 1, 2-dichloroethane, using 2.0 mol% of catalyst.
b: Determined by HPLC analysis using a Chiralcel OD-R chiral column.
c: Determined by polarimetry and the reported value of R, $[\alpha]_D^{20}$ -23(c 1, CCl$_4$).

changes from H to CH_3 or Ph, the enantioselectivities decreased significantly. So, *cis*-disubstituted olefins should give the highest *ee* value. It was also found that poor enantioselectivity was obtained when R_1= CH_3, R_2=R_3=H. So, substitution at the proximal position of the double bond appeared to be disadvantageous for the enantioselectivity.

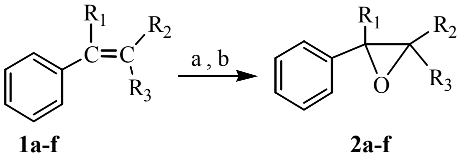
In conclusion, the catalyst of $Fe(dcm)_3$ is found to be efficient for the asymmetric epoxidation of some styrene analogues. Further attempts of application of this approach for other asymmetric reactions are under investigation.

Table 2 The influence of temperature on the asymmetric epoxidation of styrene

Entry	Temperature (℃)	Conversion (%)	Yield(%)		*ee* (%)	Config.
			2	**3**		
1	0	30	18.1	6	87.3	S
2	10	74	46.3	6	83.9	S
3	20	89	69.7	7	80.6	S
4	30	100	89.7	7	78.1	S
5	40	100	85.3	10	69.5	S
6	50	100	73.4	14	53.7	S

Reactions were performed in 1, 2-dichloroethane using 2.0 mol % of catalyst and 2-ethylbutyraldehyde as sacrificial aldehyde.

Scheme 3



a. $Fe(dcm)_3$; b. aldehyde + O_2

Table 3 Enantioselective epoxidation of styrene analogues **1a-f** catalyzed by Fe $(dcm)_3$[a].

Product	R_1	R_2	R_3	Yield (%)	*ee* (%)[b]
2a	H	H	H	89.7.	78.1
2b	H	CH_3	H	91.4	47.5
2c	H	H	CH_3	79.3	85.3
2d	H	Ph	H	62.4	57.8
2e	H	H	Ph	56.5	91.6
2f	CH_3	H	H	50.8	54.8

a: Reactions were performed in 30℃ 1, 2-dichloroethane using 2.0 mol %of catalyst and 2-ethylbutyraldehyde as sacrificial aldehyde.

b: Determined by HPLC with Chiralcel OD-R chiral column.

Experimental

Synthesis of Fe(dcm)$_3$: To a stirred mixture of Hdcm (30 mmol) in THF-MeOH(1/1, 100 mL), an aqueous solution of FeCl$_3$ (10.0 mol, 50 mL) was added over 20 min, then stirring was continued for another 2 h at 40 ℃. Precipitated reddish-brown solid was filtered and washed with MeOH and water. Recrystallization from MeOH gave reddish solid (98% yield). m.p. 292-294℃, $[\alpha]_D^{25}$ +26.4(c 4.5, CCl$_4$), ^{1}HNMR(CDCl$_3$, δ ppm): 5.13(s, 3H, CH=), 1.88-2.21(m, 6H, CH), 1.43 (s, 18H, CH$_3$), 1.09 -1.38 (m, 24H, CH$_2$), 0.33 (d, 18H, J=6Hz, CH$_3$), -1.18 (s, 18H, CH$_3$), -1.57 (s, 18H, CH$_3$), IR υ(KBr, cm^{-1}): 1545.5 (C=O), 1501.7 (C=C); Anal. Calcd for $C_{63}H_{105}O_6Fe$: C, 74.59; H, 10.43. Found: C, 74.51; H, 10.38.

General procedure for asymmetric epoxidation: A mixture of styrene analogue (3.0 mmol), Fe(dcm)$_3$ (0.06 mmol, 2.0 mol %), 2-ethylbutyraldehyde (9.0 mmol) in 1, 2-dichloro ethane(10 mL) was stirred under atmospheric pressure of oxygen at 30℃ for 10 h. The reaction mixture was washed with saturated aqueous NaHCO$_3$ solution, and after drying over anhydrous sodium sulfate, solvent was removed *in vacuo*. Purification of the residue by column silica gel chromatography afforded the chiral styrene analogue oxide.

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