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Asymmetric Mn(III)-Salen Catalyzed Epoxidation of Unfunctionalized Alkenes with Tetrabutylammonium Monopersulfate

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Abstract: Asymmetric Mn(III)-salen catalyzed epoxidation of simple *cis*-disubstituted and trisubstituted alkenes in mild conditions was performed using tetrabutylammonium monopersulfate (Bu_4NHSO_5) as the oxidant together with *N*-methylmorpholine *N*-oxide as an additive. Particularly high yields of epoxides (up to 97 %) and good enantiomeric excesses (ee up to 93 %) were obtained in the epoxidation of 2,2-dialkylchromenes and trisubstituted alkenes.

Keywords: Asymmetric reactions; Epoxidation; Catalysts

Chiral (salen)Mn(III) complexes are efficient and practical catalysts for the asymmetric epoxidation of various *cis*-disubstituted, tri- and tetrasubstituted alkenes.[1-3] Most of the epoxidations have been conducted using iodosylbenzene[2] or NaOCl[3] as the oxygen donor. Other common oxidants that have been explored with catalysts like **1** and **2** include *m*CPBA,[4] molecular oxygen,[5] dimethyldioxirane,[6] H_2O_2,[7] and periodates.[8] Recently, potassium monopersulfate (Oxone®, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used in the asymmetric epoxidation of 2,2-dialkylchromenes.[9]

Oxone is a strong, cheap and versatile oxidising agent that has earlier been studied in metalloporphyrin-catalyzed oxidations.[10] It is an efficient single oxygen atom donor since it contains a non-symmetrical O-O bond which is heterolytically cleaved during the oxidation cycle catalyzed by transition metal complexes (e.g. porphyrins, salen compounds). It has some disadvantages: it is insoluble in organic solvents, buffering is needed due to its acidity, and it sometimes bleaches the metal catalysts and donor ligands during oxidation reactions. On the other hand, it has recently been succesfully applied to the asymmetric epoxidation of *trans*-alkenes using chiral ketones as catalysts.[11] Tetrabutylammonium monopersulfate (Bu_4NHSO_5) is a solid easily prepared from commercially available Oxone.[12,13] It is readily soluble in various organic solvents and usually used in CH_2Cl_2 for the mild oxidation of sensitive compounds.[12,14] It has also been used in oxidations catalyzed by transition metal complexes with varying results.[15]

Here tetrabutylammonium monopersulfate was used to epoxidize simple unfunctionalized alkenes catalyzed with (salen)Mn(III) catalysts **1** and **2**. Monopersulfate was prepared by two similar methods from Oxone and Bu_4NHSO_4.[12,15a] The original procedure by Trost et al. gave a product with Bu_4NHSO_5 content of 37 % (the rest consisting of Bu_4NHSO_4 and $[Bu_4N]_2SO_4$) and the modification of Campestrini et al. afforded

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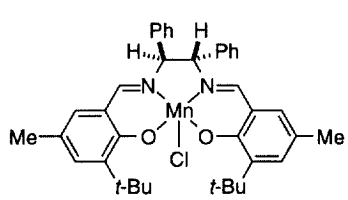
Bu_4NHSO_5 with a purity of about 90 %.[16] The epoxidations were typically performed in CH_3CN containing the substrate, oxidant, *N*-methylmorpholine *N*-oxide (NMO), and salen in a ratio of 1: 1.5: 1: 0.07.[17] The function of NMO is to act as a proximal ligand to the metal.[1,10] The results are summarized in Table 1.



1

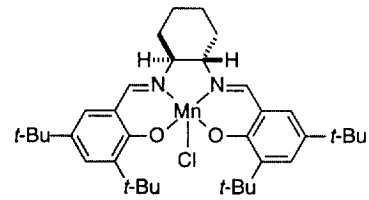


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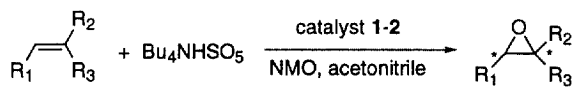
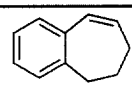
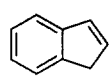
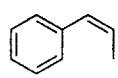
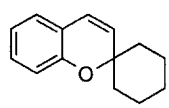
Table 1. Epoxidation of Unfunctionalized Alkenes with Bu_4NHSO_5 and Catalysts **1**-**2**[a]



entry	alkene	catalyst	temp. (°C)	time (h)	yield (%)[b]	ee (%)[c]
1		**1**	2	1	59	89 (81)[d]
2	"	**1**	-18	1.5	72	90
3[e]	"	**1**	-18	2.5	74	88
4[f]	"	**1**	-18	1.75	72	84
5	"	**2**	2	2.5	52	72
6		**1**	-18	1	75	72
7		**1**	-18	1	72[g]	87[h]
8		**1**	-18	1.25	96	90
9		**1**	-18	1	97	93
10	"	**2**	2	2.5	86	84

a) Reactions were carried out in CH_3CN (2 ml) with molar ratio of alkene: oxidant: NMO: catalyst= 1: 1.5: 1: 0.07.
b) Yield of the isolated epoxide.
c) Determined by ^1H NMR analysis (200 MHz) in the presence of $Eu(hfc)_3$.
d) Value in parenthesis is for the reaction using 37 % Bu_4NHSO_5 as the oxidant.
e) Reaction was conducted in CH_2Cl_2.
f) Reaction was performed using 25 mol-% of NMO.
g) A mixture of *cis*- and *trans*-epoxides in a ratio of 8:1.
h) ee of the *cis*-epoxide.

First, the epoxidation of 5,6-dihydro-5*H*-benzocycloheptene was studied in different reaction conditions using the catalyst **1**. The reaction proceeded smoothly at 2 °C giving the epoxide of 89 % ee in 59 % yield (entry 1) using monopersulfate prepared by the method of Campestrini et al. (90 % Bu_4NHSO_5). Oxidation with 37 % Bu_4NHSO_5 was equally fast producing an epoxide with somewhat lower ee of 81%. For this reason rest of the reactions were conducted with the purer oxidant. Lowering the reaction temperature from 2 °C to -18 °C increased the yield (72 %) but had practically no effect on the ee of the epoxide (entry 2). Conducting the epoxidation in CH_2Cl_2 gave identical results than reactions in CH_3CN, only the reaction time was increased from 1.5 h to 2.5 h at -18 °C (entry 3). When the reaction was performed using substoichiometric amount of the additive NMO (25 mol-%) the ee was slightly reduced (entry 4).

Surprisingly, when the epoxidation of benzocycloheptene was catalyzed by commercially available "Jacobsen's" catalyst **2** the reaction proceeded slower and the ee of the epoxide dropped considerably compared to the reaction catalyzed by **1** (from 89 % to 72 %, entries 1 and 5). The reason for this difference is not clear, probably the catalyst **2** is partially deactivated during the catalytic cycle by some unknown mechanism (see ref. 15a for similar comments). With some other oxidants (e.g. H_2O_2) both of these catalysts give comparable yields and ee's in epoxidation reactions.[7b]

Epoxidation of other di- and trisubstituted aromatic alkenes also proceeded smoothly with high yields and enantioselectivity. Only the epoxidation of indene gave moderate ee (entry 6). The stereoselectivity obtained in the epoxidation of *cis*-β-methylstyrene (cis/trans= 8) was at the same level as obtained earlier with *m*CPBA/NMO-system at low temperatures (entry 7).[5] Particularly useful values (yield, ee) were obtained for electron-rich substrates (entries 8-9). Here was also seen the difference in reactivity between the catalysts **1** and **2**, again catalyst **1** giving both higher yield and ee in the epoxidation of 1,1-diphenyl-1-propene (entry 10).

In conclusion, tetrabutylammonium monopersulfate was found to be a useful oxidant in Mn(III)-salen catalyzed asymmetric epoxidations. It might find more general use since it is readily soluble in various organic solvents (compare with e.g. Oxone, PhIO). For example, comparing the oxidation of spiro[chromen-2,1'-cyclohexane] by Bu_4NHSO_5/NMO with that of Oxone using catalyst **1** (see ref. 9), shows that the system presented here offers considerably milder reaction conditions. Based on the promising results above, further studies of other monopersulfates soluble in organic solvents acting as potential oxidants in asymmetric epoxidation of alkenes is underway.

Acknowledgement

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16. Monopersulfates were titrated iodometrically using the procedure in ref. 12.
17. General experimental procedure: To a cooled solution of alkene (0.4 mmol), NMO (0.4 mmol), and **1** (0.028 mmol) in CH_3CN (2 ml) was added precooled solid Bu_4NHSO_5 (0.6 mmol) in two portions during 20 min. The reaction was monitored by TLC. After completion, the reaction was quenched with excess Me_2S. Solid K_2CO_3 was added, the mixture was filtered, and the filtrate concentrated. The crude product was purified by flash chromatography and the ee of the epoxide was determined by ^1H NMR in the presence of $Eu(hfc)_3$.