

Short Communication

Enantioselective oxidation of racemic secondary alcohols catalyzed by chiral Mn(III)-salen complex with sodium hypochlorite as oxidant



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ABSTRACT

Chiral Mn(III)-salen complex catalyzed oxidative kinetic resolution (OKR) of secondary alcohols has been achieved with cheap and easily available sodium hypochlorite (NaClO) as oxidant. The novel protocol is very efficient for the OKR of a variety of secondary alcohols at room temperature.

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Chiral Mn(III)-salen complex

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1. Introduction

Enantiomerically pure secondary alcohols are useful chiral auxiliaries and intermediates in the pharmaceutical, agrochemical, and fine chemical industries [1–3]. Generally, they have been prepared by many methods, including asymmetric hydrogenation of prochiral ketones catalyzed by metal complexes [4,5], enzymatic kinetic resolution of racemic secondary alcohols through acylation–deacylation reactions [6], and nonenzymatic kinetic resolution [7]. Among the known processes, the oxidative kinetic resolution (OKR) of racemic alcohols to obtain enantioenriched alcohols is an attractive and efficient method [8–17]. Many catalysts or catalytic systems with excellent or good resolution results, including (–)-sparteine–Pd(II), sparteine analogues–Pd(II), N-heterocyclic carbene(NHC)–Pd(II), chiral difunctional–Ir complexes, chiral(ON)–Ru(salen) complexes and chiral Mn(III)–salen complexes, have been developed [18]. The OKR of alcohols with chiral Mn(III)–salen complexes as catalysts and (diacetoxyiodo) benzene (PhI(OAc)₂) as terminal oxidant in the presence of potassium bromide was first established by Xia et al. in 2003 [19–22]. The system for the OKR of alcohols has the advantages of easy availability and handling of the chiral Mn(III)–salen complexes. However, it also has the disadvantage of using stoichiometric PhI(OAc)₂ as oxidant which is poor in atom economy, very expensive and unfriendly to the environment. Recently, N-bromosuccinimide (NBS) was used as oxidant to replace PhI(OAc)₂ in the chiral Mn(III)–salen complex catalyzed OKR of alcohols and proved very efficient for the oxidative kinetic resolution of a variety of secondary alcohols, including ortho-substituted benzylic alcohols [23,24].

Corey and his co-workers [25] made detailed investigations on the mechanism of Xia's system for the OKR of alcohols. Some of the salient features of the proposed mechanism are as follows: (1) A positive bromine species Br₂ or HOBr is generated under the reaction conditions by oxidation of bromide ion with PhI(OAc)₂. (2) It is the positive bromine species that oxidizes the Mn(III)–salen complex to a dibromo–Mn(V) species. (3) The dibromo–Mn(V) species enantioselectively converts one enantiomer of the racemic alcohols to a ketone and left another alcohol. These conclusions are supported by the facts that PhI(OAc)₂ and KBr can be replaced by Br₂ or HOBr as the stoichiometric oxidant in the enantioselective oxidation. Although highly enantioselective oxidations can be carried out with Br₂ or HOBr as stoichiometric oxidant instead of PhI(OAc)₂, using stoichiometric Br₂ or HOBr as the oxidant will suffer from the inherent disadvantages of low atom efficiency (less than 50%) of bromine and environmental pollution due to one equivalent of HBr as by-product being produced, and inconvenience in use from the perspective of synthesis. In light of the oxybromination reaction developed recently [26–29] and Corey's mechanism about Xia's system for the OKR of alcohols, we envisioned a new system with catalytic amount of Br₂ as cycling agent and stoichiometric NaClO as oxidant for the OKR of alcohols catalyzed by the Jacobsen's chiral Mn(III)–salen complex [30] (Fig. 1) in the biphasic CH₂Cl₂/H₂O medium in the presence of KOAc. Herein, we report the successful resolution examples by employing the cheap and convenient system.

2. Experimental

2.1. Materials and apparatus

Hydrogen peroxide and sodium hypochlorite were obtained from Tianjin Fuchen Chemical Reagent Factory, China. All the chemicals

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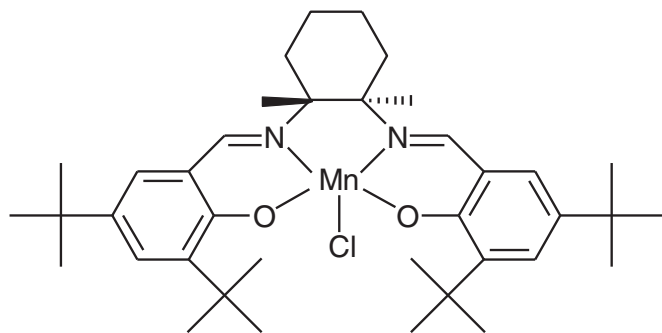


Fig. 1. Structure of Jacobsen's chiral Mn(III)-salen complex.

were used as received. The secondary alcohols were obtained from Alfa Aesar China (Tianjin) Co., Ltd. Samples were analyzed on a Shandong Lunan Ruihong Gas Chromatograph (SP-6800A) equipped with a hydrogen flame detector and a chiral column (Cyclodex- β , 30 m $\times$ 0.25 mm (i.d.), 0.25 μ m). HPLC experiments were performed on Agilent-1260 plus (Daicel Chemical Industries, Tokyo Japan) equipped with a 1260-DAD detector and a normal Daicel Chiralcel OD-H column, ϕ 4.6 $\times$ 250 mm.

2.2. Catalytic procedure

In a typical process, a mixture of ($\pm$)-1-phenylethanol (0.122 g, 1 mmol), chiral Mn(III)-salen complex (0.0127 g, 2 mol%), Br₂ (4.1 μ L, 8 mol%), KOAc (0.1962 g, 2 mmol), CH₂Cl₂ (2.0 mL), and water (4.0 mL) was magnetically stirred in a 10-mL two-necked flask at 20 °C. The oxidant NaClO (0.289 g, 0.80 mmol) was then added slowly within 40 min, and the reaction was monitored by GC/HPLC equipped with a suitable chiral column.

2.3. Analysis of the reaction mixture

After the addition of ($\pm$)-1-phenylethanol, chiral Mn(III)-salen complex, CH₂Cl₂, H₂O and Br₂, 10 μ L of the organic phase was removed and put into a 10 mL of volumetric flask, the mixture 1 was dissolved with mobile phase to constant volume. After the addition of NaClO, another 10 μ L of the organic phase was removed and put into a 10 mL of volumetric flask, the mixture 2 was dissolved with mobile phase to constant volume. The conversion of ($\pm$)-1-phenylethanol was determined by HPLC with single-point external standard method. HPLC conditions: Hexane/*i*-ProH = 95: 5 (v/v), 1.0 mL/min, 210 nm, 20 °C.

$$\text{Conversion(\%)} = \frac{\text{the peak area of mixture 1} - \text{the peak area of mixture 2}}{\text{the peak area of mixture 1}} \times 100\% \quad (1)$$

$$\text{ee(\%)} = \frac{R-S}{R+S} \times 100\% \quad (2)$$

$$k_{\text{rel}} = \frac{\ln(1-\text{Conv})(1-\text{ee})}{\ln(1-\text{Conv})(1+\text{ee})} \quad (3)$$

Besides, the conversion of ($\pm$)-1-phenylethanol was also determined by GC with area normalization method. GC conditions: column temperature: 100 °C, injector 220 °C, detector: 220 °C, pressure: 0.05 MPa.

3. Results and discussion

In principle any oxidants able to oxidize HBr to Br₂ are candidates for the chiral Mn(III)-salen complex catalyzed OKR of alcohols. From a

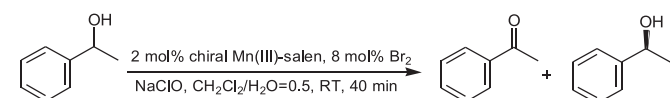
“green” chemistry perspective [31,32], the best choice would be either molecular oxygen or hydrogen peroxide since water would be the only by-product in oxidation. Besides, molecular oxygen, as the most abundant and cheapest oxidant, was successfully used to replace PhI(OAc)₂ in the oxidation of alcohols with Br₂ as active oxidant [33]. Additionally, the cheap and easily available hydrogen peroxide was also applied to the oxidation of HBr in literature [34,35]. Therefore, we first tested molecular oxygen and hydrogen peroxide respectively as oxidants in the OKR of α -phenylethanol. It is disappointing that no enantioselective oxidation occurred in both cases (Table 1, entries 1, 2). Then another oxidant *tert*-butyl hydroperoxide (TBHP) was tried again, a failure was received too (Table 1, entry 3). Finally, we used sodium hypochlorite as oxidant to carry out the reaction, a delightful result was obtained (Table 1, entry 4). In the initial experiment the enantioselectivity reached about 100% when the conversion of α -phenylethanol was kept 62.8%. Though sodium hypochlorite is not good compared to molecular oxygen and hydrogen peroxide as oxidant from an environmental point of view, it is still a good choice due to its cheapness and easy availability. Besides, the main by-product in the reaction is sodium chloride, which can be recycled in large scale chemical process. Only NaClO as oxidant is efficient in the reaction can be explained as NaClO can oxidize Br[−] to Br₂ in the catalytic cycle in basic medium, however, acidic medium is necessary for the same transformation with the other tested oxidants.

The initial experimental results indicated that NaClO was feasible to replace PhI(OAc)₂ in the OKR of α -phenylethanol, therefore, we investigated it in detail. Corey [25] pointed that slow addition of oxidant to prevent the detrimental build up of HBr was very important in the chiral Mn(III)-salen complex catalyzed OKR of alcohols. Thus, we inspected the effect of the addition time of NaClO on the OKR of α -phenylethanol. The results are shown in Fig. 2. It can be seen that both the conversion and the enantiomeric excess increased with extending the addition time of NaClO as expected, when the addition time of NaClO was 40 min, both of them reached their maximums, and did not increase with prolonging the addition time of NaClO. Thus, we chose 40 min as the suitable addition time of NaClO in the subsequent experiments.

The OKR of various secondary alcohols was explored with the novel catalytic system. The results are summarized in Table 2.

It can be observed from Table 2 that most of the tested substrates were smoothly resolved with good to excellent enantioselectivity comparable to those obtained from Xia's catalytic system in literature [19–22]. Similar to the results in literature [19–22], the OKR of α -phenylethanol and its derivatives including 1-(4-fluorophenyl) ethanol, 1-(4-chlorophenyl) ethanol, 1-(4-bromophenyl) ethanol, 1-(4-methylphenyl) ethanol, proceeded readily with excellent

Table 1
Choice of oxidant with α -phenylethanol as substrate.^a



Entry	Oxidant	Dosage (mmol)	Conv (%) ^b	ee (%) ^c	k _{rel} ^d
1	O ₂ -NaNO ₂ -Br ₂	Oxygen ball	3.37	13.48	−1.94
2	H ₂ O ₂	0.70	5.57	7.34	−9.88
3	TBHP	0.80	26.37	12.06	2.26
4	NaClO	0.80	62.85	~100	–

^a Reaction conditions: α -phenylethanol 1 mmol, Mn(III)-salen 0.02 mmol, Br₂ 0.08 mmol, KOAc 2 mmol, CH₂Cl₂ 2 mL, H₂O 4 mL, reaction temperature 20 °C, reaction time 40 min (the oxidants were added within 40 min).

^b The conversion was determined by GC with area normalization method.

^c Determined by GC with a chiral column.

^d k_{rel} = ln[(1 − Conv)(1 − ee)]/ln[(1 − Conv)(1 + ee)].

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