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# Easy separation and reutilization of the Jacobsen's catalyst in olefin oxidation

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ABSTRACT

A new method for recycling the Jacobsen's catalyst used for the catalytic oxidation of R-(+)-limonene and *cis*-ethyl cinnamate at room temperature by *in situ* generated dimethyldioxirane (DMD) as oxidizing agent is presented. Neither the immobilization of the catalyst to the solid support nor modification of its chemical structure is involved in this method. Therefore, the excellent catalytic properties of the Jacobsen's catalyst could be retained. Limonene diepoxide was the main product of the oxidation of R-(+)-limonene, whereas a single epoxide with good enanantioselectivity (78% ee) was obtained in the asymmetric oxidation of *cis*-ethyl cinnamate. On the other hand, R-(+)-limonene showed to be more reactive than *cis*-ethyl cinnamate. In both cases, the catalyst was recovered and recycled without appreciable loss of its initial catalytic activity.



## 1. Introduction

The Jacobsen's catalyst is one of the most important catalysts for olefin asymmetric epoxidation because of its high asymmetric induction to give pure optical epoxides [1]. It is a Mn(III) salen complex, which consists of a dissymmetric diimine bridge derived from a C2-symmetric 1,2-diamine and bulky substituents on the 3- and 3′-positions of the salicylide ligand. The optimal balance of steric and electronic salen ligand properties is apparently the cause of its high asymmetric induction [2]. However, the industrial application of the Jacobsen's catalyst is limited because it is difficult to separate from the reaction products [3]. Additionally, its poor stability due to oxidative degradation avoids its reutilization [3]. In order to overcome these drawbacks, various research groups have reported the immobilization of the Jacobsen's catalyst either to an inorganic or organic solid support [4]. The immobilization by covalent bond, generally leads to high stability towards leaching. However, this immobilization procedure is quite laborious and the resulting material exhibits less catalytic activity than the free catalyst [5]. It has been recognized that the excellent asymmetric induction of Jacobsen type catalysts in homogeneous phase is related to the adoption of an appropriate geometrical configuration [6]. Apparently, the solid support negatively influences the desired configuration of the immobilized catalyst [7]. On the other hand, the commonly used oxidizing agents such as sodium hypochlorite (NaOCl) and iodosylbenzene (PhIO) have showed to degrade the catalyst, which represents a clear disadvantage for catalyst reusability [7].

As previously described [5–7], improvement of catalyst stability is expected for the heterogeneous asymmetric oxidation of olefins using the un-immobilized Jacobsen's catalyst under mild reaction conditions. Recently, we found [8] that the Jacobsen's catalyst could be recovered and reused for the enantioselective epoxidation of *cis*-ethyl cinnamate using *in situ* generated dimethyldioxirane (DMD) as oxidizing agent.

The strategy was to vary the solubility of the catalyst during reaction. This work is an extension of our previous work on the enantioselective epoxidation of *cis*-ethyl cinnamate [8]. Herein, we compare the effectiveness of the recovery and reuse of the catalyst for the oxidation of R-(+)-limonene and *cis*-ethyl cinnamate. The asymmetric oxidation of *cis*-ethyl cinnamate is the key step for preparing Taxol® an anti-carcinogenic drug [9] and the oxidation of R-(+)-limonene to oxygenated monoterpenes is of great importance for preparing flavor, fragance and perfume compounds [10].

## 2. Experimental

### 2.1. Materials

R-(+)-limonene (99%) was purchased from Aldrich. The Jacobsen' catalyst and *cis*-ethyl cinnamate were prepared by conventional methods [11,12]. The reagents and solvents used in the synthesis of these materials were used as received. 1,2-Diaminocyclohexane (99% mixture *cis*/*trans*), 3,5-di-tert-butylsalicylaldehyde, L-tartaric acid (99%), potassium carbonate, manganese (II) acetate tetrahydrate, lithium chloride, ethyl phenylpropiolate, quinoline, Lindlar's catalyst, ethanol, hexane and hexene were purchased from Aldrich.

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Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and acetone were purchased from Aldrich and used to generate *in situ* dimethyldioxirane (DMD).

### 2.2. Characterization

Infrared Fourier transform spectroscopy (FT-IR) data were taken at room temperature on a Nicolet Avatar 330 spectrophotometer using standard KBr techniques. Thermal analysis (TGA) was performed in a TGA 2950 apparatus with a heating rate of 1 K/min in the presence of ambient air, using $Al_2O_3$ crucibles; $\alpha$-$Al_2O_3$ was used as reference material. The electronic spectra in the UV–vis region were recorded in powder samples using a Lamda 4B Perkin Elmer spectrophotometer.

A gas chromatograph (GC), Agilent Technologies 7890A equipped with a DB-1 capillary column (50 m long, 0.32 mm ID and 1.20 μm film thickness) and a FID detector was used for the analysis of solvent purity, olefin and oxidation products. Ultra high pure helium was used as carrier gas (30 mL/min). The injection port temperature was kept at 300 °C. For R-(+)-limonene the column temperature was programmed between 80 and 140 °C while for *cis*-ethyl cinnamate it was kept isothermal at 140 °C. The area normalization method was used to determine conversion and selectivity. The enantiomeric excess (ee) for the single epoxide derived from *cis*-ethyl cinnamate epoxidation was determined by GC using a chiral capillary column, i.e. Betadex GTA (60 m long, 250 μm ID and 0.25 μm film thickness). In this case, a commercially available 3-ethyl-phenylglycidate (*cis*/*trans* = 10/90, Aldrich) racemic mixture was used. In the case of the chiral epoxides derived from R-(+)-limonene, (+)-limonene oxide (97%, mixture of *cis* and *trans*, Aldrich) was used. Limonene diepoxide was prepared by oxidation of (+)-limonene oxide using *m*-chloroperbenzoic acid as oxidizing agent and confirmed by GC–MS. The optical configuration was assigned by comparing the chromatogram of our products with those of *cis*-ethy cinnamate isomers available in literature [13,14].

### 2.3. Catalytic tests

Catalytic oxidation of *cis*-ethyl cinnamate and R-(+)-limonene with *in situ* generated DMD was carried out in three necked magnetically stirred round-bottom flasks. All the reactions were performed at atmospheric pressure and room temperature as follows: substrate (1 mmol), acetone (4 mL) and catalyst (0.05 mmol) were first introduced into the round-bottom flasks. Then, an Oxone® aqueous solution (2 mmol of Oxone® in 4 mL water) was added dropwise maintaining the pH of the reaction mixture around 8.0 by means of a $NaHCO_3$ aqueous solution (5 wt%). DMD formed *in situ* from the reaction between $KHSO_5$ (active component of Oxone®) and acetone (Fig. 1) [15]. After the total addition of the oxygen source, stirring was stopped. The resulting solid (catalyst and inorganic salts) was separated by centrifugation and thoroughly washed with de-ionized water to remove inorganic salts. The resulting solid (catalyst) was dissolved in acetone prior to its reusing. The liquid phase was cooled at 0 °C in order to remove additional solid. The remaining liquid phase was extracted with $CH_2Cl_2$. The aqueous phase was discarded off, while the organic phase was dried over sodium sulphate and the solvent partially removed by vacuum. An aliquot was taken from concentrated solution with a hypodermic syringe and directly analyzed by GC–MS. The products were identified using commercially available standard samples and confirmed by mass spectrometry. Blank experiments under the same experimental conditions but, in the absence of catalyst or in the absence of oxidant were also performed. Also, isolated yields of predominant epoxide product for each substrate were calculated. Thus, the epoxide originating from *cis*-ethyl cinnamate oxidation was purified by short-path distillation (110 °C and 0.5 mmHg), while in the case of R-(+)-limonene, diepoxide was colleted at 140 °C and 0.5 mmHg.

## 3. Results and discussion

### 3.1. Characterization

One of the highly attractive aspects of the Jacobsen's catalyst is that it can be easily synthesized from readily available, low cost starting materials. The first step is a chiral resolution of (R,R)-1,2-diaminocyclohexane from a mixture of *cis* and *trans* isomers of the diamine. This is accomplished by using L-(+)-tartaric acid to form diastereomeric salts of the diamine. The relatively low aqueous solubility of the R,R diamine salt allows it to be crystallized in high enantiomeric purity. In the second step, the tartrate salt of (R,R)-1,2-diaminocyclohexane is reacted with two molar equivalents of 3,5-di-tert-butylsalicylaldehyde to form the salen ligand. Finally, reaction of the salen ligand with manganese (II) acetate in the presence of lithium chloride and atmospheric oxygen forms [(R,R)-N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato(2-)] manganese (III) chloride, which corresponds to the Jacobsen's catalyst [10]. This complex is soluble in most common organic solvents, but insoluble in water. In order to obtain more details on the structure of complex, both the salen ligand and the Jacobsen's catalyst, were characterized by FT-IR, UV–vis and TG–DTA. These results showed to be in good agreement with the

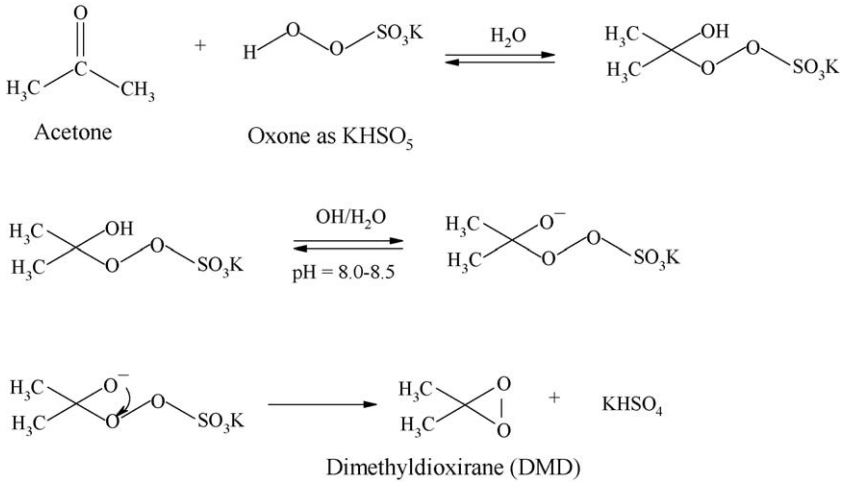


**Fig. 1.** Formation of dimethyldioxirane from acetone and $KHSO_5$ under basic conditions [15].