



# Salen manganese (III) complexes as catalysts for R-(+)-limonene oxidation

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## ARTICLE INFO

### Article history:

Received 9 May 2009

Received in revised form 18 October 2009

Accepted 24 October 2009

Available online 30 October 2009

### Keywords:

R-(+)-limonene

Epoxides

Jacobsen-type catalysts

Homogeneous catalyst

Recoverable catalyst

## ABSTRACT

The epoxidation of R-(+)-limonene using *in situ* generated dimethyldioxirane (DMD) as the oxidizing agent and four Jacobsen-type catalysts ((R,R)-Jacobsen, (S,S)-Jacobsen, racemic Jacobsen and achiral Jacobsen) was examined. The effect of the amount of  $\text{KHSO}_5$  and acetone in the catalyzed and uncatalyzed reaction was also assessed. The main reaction products were diepoxide and endocyclic monoepoxide. In the absence of catalyst, the amount of  $\text{KHSO}_5$  did not significantly influence conversion and selectivity. The catalyst can be segregated to a different phase and separated from the reaction media when the amount of  $\text{KHSO}_5$  is above the stoichiometric ratio, R-(+)-limonene/ $\text{KHSO}_5 = 0.5$  mmol/mmol, and acetone/mmol R-(+)-limonene = 2 mL/mmol. However, when the amount of  $\text{KHSO}_5$  is below the stoichiometric ratio (R-(+)-limonene/ $\text{KHSO}_5 = 1.5$  mmol/mmol) the catalyst is difficult to separate. Under the reaction conditions of this study, when the catalyst is segregated, no effect of the catalyst chiral center, (R,R)-Jacobsen or (S,S)-Jacobsen, was found on conversion and selectivity. Additionally, the (R,R)-Jacobsen's catalyst proved to be very stable to oxidative degradation.

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## 1. Introduction

Limonene derivatives functionalized with oxygen are important intermediates in the preparation of pharmaceuticals, food additives, and agrochemicals [1]. Fig. 1 shows the main products from the oxidation of limonene which are classified in two groups. The first group comprises products from the epoxidation of the double bonds denoted as epoxides [2]. Additionally, epoxides can be classified as monoepoxides if a double bond is oxidized and diepoxides if both double bonds are oxidized. If the double bond between carbons 1 and 2 is oxidized, the monoepoxide corresponds to the endocyclic epoxide. If the double bond between carbons 8 and 9 is oxidized, the resulting monoepoxide is the exocyclic epoxide [2]. The second group corresponds to allylic oxidation products, which include carveol and carveone [2].

Due to the existence of a chiral center in the chemical structure of limonene (carbon 4, Fig. 1), this compound has two enantiomers with optical configurations R and S [3]. Orange peels are the main source of R-(+)-limonene, while lime peels mostly contain S-(-)-limonene [4]. Either limonene enantiomer has eight optically pure epoxides [4]. Fig. 2 shows the chemical structure of these epoxides and their corresponding optical configuration. It is important to note that each monoepoxide has two isomers (*cis/trans*) known as diastereomers. Just like any pair of enantiomers, the cyclic diastereomers *cis/trans* show different behavior when interacting

with a biological receptor, mainly due to the orientation of the substituents [5]. This is how a diastereomer can be effective in the treatment of an illness; while its counterpart may be inactive or even produce opposite effects. For this reason, there is much interest on the development of efficient processes for obtaining optically pure epoxides [6].

The Jacobsen–Katsuki epoxidation is used in the production of optically pure epoxides [7]. The success of this method is based on the use of manganese (III)–salen complexes, as catalysts. Fig. 3 shows the chemical structure of the Jacobsen's catalyst [7]. The most common solvents used are dichloromethane and acetonitrile and the most used oxidizing agents are sodium hypochlorite, iodosylbenzene, and *meta*-chlorobenzoic acid. In spite of the satisfactory results achieved with this method (enantiomeric excess  $\geq 95\%$ ), no industrial process still exists because reaction products and catalyst are in the same phase and are difficult to separate by physical–mechanical methods [8]. Therefore, various methods for the heterogenization of Jacobsen–Katsuki type catalysts have been proposed. The immobilization of the catalyst on the surface of a solid (support) by covalent chemical bond is mostly used [9]. With this method, the complete separation of the catalyst from the reaction products has been proved. However, no successful immobilization method has been established that keeps the catalytic properties of the homogeneous catalyst or the preservation of the initial catalytic activity of the immobilized catalyst [10].

It is generally recognized that the solid support prevents the geometric reception of the active catalytic species attained in a homogeneous phase, which is interpreted as a poor chiral

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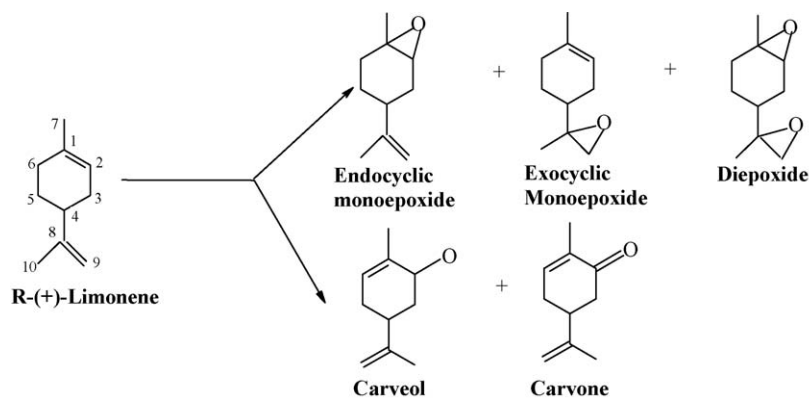


Fig. 1. Main oxygenated products from limonene.

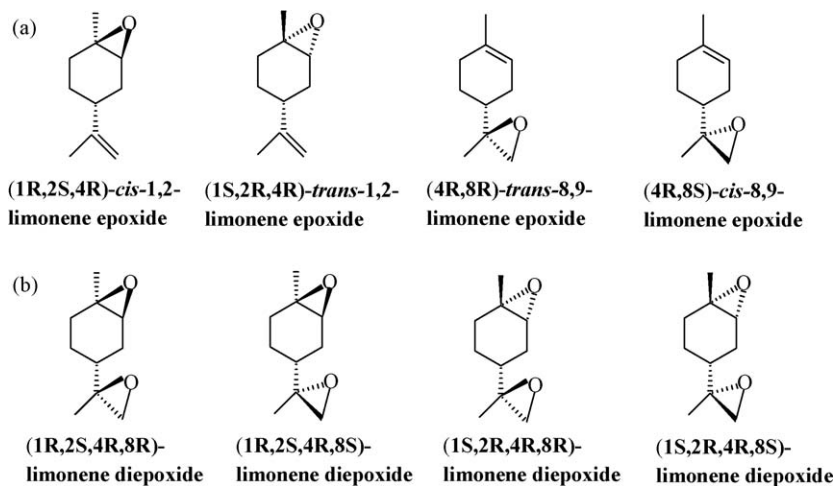


Fig. 2. Epoxides derived from R-(+)-limonene: (a) monoepoxides; (b) diepoxides.

communication between the catalyst and the olefin [11]. On the other hand, it has been established that oxidizing agents such as sodium hypochlorite and iodosylbenzene promote the deactivation of the catalyst because of the oxidative degradation of the salen ligand [11]. To overcome these difficulties, the use of dimethyldioxirane (DMD) generated *in situ* as an oxidizing agent

improves the stability of the catalyst because of the moderate oxidation conditions that can be attained [12,13]. Additionally, the catalyst initially soluble in the reaction medium, can be segregated depending on reaction conditions.

In this paper we report on the asymmetric oxidation of R-(+)-limonene using *in situ* generated DMD as oxidizing agent in the

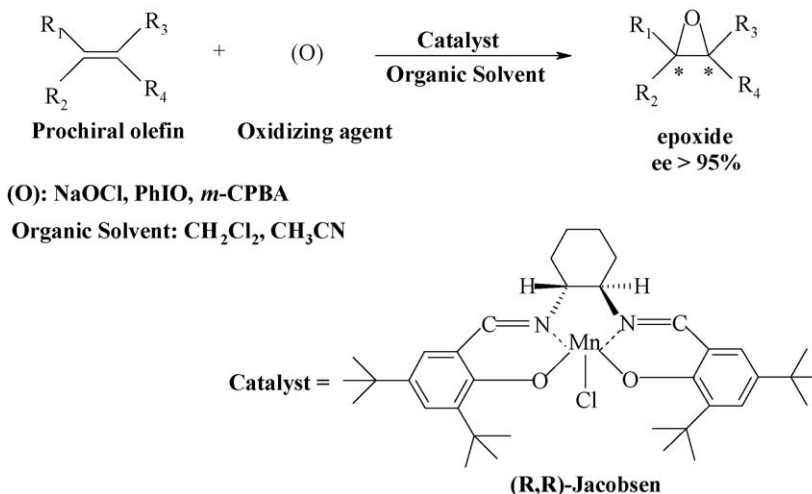


Fig. 3. Jacobsen asymmetric epoxidation.

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