Tetrahedron 72 (2016) 1–16

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report 1097

Recent advances and perspectives in the manganese-catalysed epoxidation reactions

K. Keerthi Krishnan, Anns Maria Thomas, Kallikkakam S. Sindhu, Gopinathan Anilkumar *

School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, 685560, India

ARTICLE INFO

Article history:
Received 18 June 2015
Available online 10 November 2015

Keywords:
Catalysis
Manganese catalysis
Epoxidation
Asymmetric epoxidation

Contents

* Corresponding author. Tel./fax: +91 481 2731036; e-mail address: anilgi1@yahoo.com (G. Anilkumar).

http://dx.doi.org/10.1016/j.tet.2015.11.003

1. Introduction

Metal-catalysed oxidation is one of the most important reactions in chemistry and biology.[1] In particular, transition metal complex-catalysed epoxidation of olefins is of increasing significance in organic synthesis since it offers effective methods of synthesis of important organic compounds that have industrial as well as medical applications,[2] and these epoxides can be readily converted to a wide variety of value added compounds.[3] Among the transition metal catalysts used for epoxidation, manganese complexes by virtue of their wide range of stable and chemically accessible oxidation states (II–V and VII) have been the subject of intense research as oxygen atom transfer catalysts.[4] In addition, manganese is catalytically active in a variety of metalloenzymes[5] and is also less damaging to the environment compared to other transition metals. This has warranted a large number of reports in the literature for manganese complexes as oxidation catalysts.[6]

Asymmetric olefin epoxidation using chiral manganese complex is an important area of research, because of the versatility of chiral epoxides as useful intermediates in the preparation of a diverse array of functional molecules[7] and also they are valuable synthetic intermediates in the development of new drugs. This evoked much interest in designing efficient catalysts for asymmetric olefin epoxidation.[8] Several chiral manganese complexes have been developed for the enantioselective epoxidation reactions.[8,9]

Many manganese-based catalytic systems involving ligand free,[10] porphyrin,[11] salen,[12] salophen,[13] carbohydrate-salen,[14] nonheme,[15] calix[4]arene,[16] *tris*-imidazole,[17] oxazoline[18] and oxazine[19] have been reported to catalyse the nonasymmetric and enantioselective epoxidation of olefins. A few reviews published in this topic are (1) the mechanisms of manganese-catalysed oxidation of alkenes with H_2O_2[20] (2) the application of manganese complexes of ligands derived from 1,4,7-triazacyclononane in oxidative catalysis[21] (3) the homogeneous chiral(salen)manganese (III)-promoted asymmetric epoxidation (AE) of olefins[22] (4) manganese and cobalt 3-oxobutylideneaminato complexes, design and application for enantioselective reactions[23] and (5) chromium- and manganese-salen promoted epoxidation of alkenes.[24] Earlier, Rose and coworkers reviewed the enantioselective epoxidation of olefins using chiral manganese porphyrin catalysts.[25]

Now-a-days, the synthesis of new polymers is intended to be used for specific tasks. For example, it is used as a tool in the preparation of controlled nanostructured and responsive surfaces with specific (multi)functionalities. These act as intermediates in the synthesis of several polymer supported catalysts, especially for solid supported manganese catalysts for olefin epoxidation. Several polymer supported manganese-catalysed olefin epoxidation reactions have been reported. Some recent examples are (1) an immobilized imidazolyl manganese porphyrin for the oxidation of olefins[26] (2) self-supported chiral polymeric Mn(III) salen complexes as highly active and recyclable catalysts for epoxidation of nonfunctionalised olefins[27] (3) immobilization of chiral(salen)manganese (III) complexes into mesoporous helical silica for asymmetric epoxidation of alkenes[28] etc. A few reviews published in this area are (1) the immobilization of chiral manganese (III) salen complexes for enantioselective epoxidation of unfunctionalised olefins[29] (2) functional micro-and nanoparticles—a possible tool for nanostructured materials[30] (3) recent progress in the heterogenization of complexes for single-site epoxidation catalysis[31] and (4) porous cryptomelane-type manganese oxide octahedral molecular sieves (OMS-2); synthesis, characterization and applications in catalysis.[32]

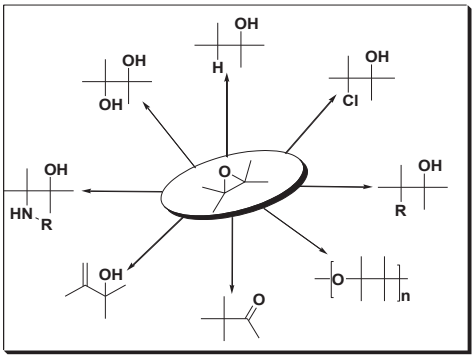
To the best of our knowledge, no review has yet been published dealing with manganese-catalysed olefin epoxidation reactions under ligand-free and in the presence of various ligand systems covering asymmetric and nonasymmetric reactions. Therefore in the present review, we discuss both the ligand-free and the ligand-based systems in manganese-catalysed olefin epoxidation covering asymmetric as well as nonasymmetric strategies focusing on the ligands used to make Mn catalysts and are conveniently classified based on the structures as they used, and not as active forms and covers the literature from 2005 to 2015.

Prior to 2005, various studies have been reported for ligand free[33] and ligand based[34] manganese-catalysed epoxidations pertaining to asymmetric as well as nonasymmetric systems. The ligand free systems offer considerable promise towards low cost catalyst systems and which are easy to operate, however such systems do pose drawbacks especially with regard to substrate scope and limited opportunity to tune selectivity and activity to enantioselective oxidations. The ligand based manganese-catalysed epoxidations generally show limitations in substrate scope and selectivity. From 2005 onwards, several modifications have been reported in both ligand free and ligand based systems including asymmetric and nonasymmetric for the epoxidations of a broad range of olefins. In the present review, we specifically focused on literature reported during this period.

It is envisaged that the oxidation state of Mn, the coordinating atoms and the geometry of the ligands influence the catalytic efficiency of the metal complex in alkene epoxidation. Therefore, we have categorized the reactions based on the oxidation state of Mn and the type of coordinating atoms.

2. Catalytic epoxidation reactions

Epoxides are important and versatile class of organic compounds and consequently selective epoxidation of alkenes is a major area of research.[35] Epoxides can be transformed into a variety of functionalized products such as alcohols, diols, aminoalcohols, allylic alcohols, ketones, polyethers etc. by reduction, rearrangement or ring opening reaction with various nucleophiles (Scheme 1).[35]



Scheme 1. Possible conversions of epoxides (R=alkyl, aryl) to useful compounds.

The epoxidation of olefins can be achieved by a variety of oxidants like H_2O_2,[15] $NaIO_4$,[36] *m*-CPBA,[37] peracetic acid,[38] sodium hypochlorite,[37] urea hydrogen peroxide (UHP),[19] iodosobenzene[15] etc. Here a concise account of new and improved methods for the construction of epoxides using ligand-free and ligand-based manganese catalysts together with various oxidants is described.

2.1. Mn(II) systems for alkene epoxidation

2.1.1. Ligand-free manganese(II)-catalysed epoxidation. One of the earliest reports for ligand-free Mn-catalysed epoxidation reaction was the use of manganese(II) salt, $MnSO_4$ with 30% aqueous