



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Full paper/Mémoire

Solvent-free epoxidation of himachalenes and their derivatives by TBHP using $[\text{MoO}_2(\text{SAP})]_2$ as a catalystMohammed Loubidi^{a,b}, Dominique Agustin^{a,c,*}, Ahmed Benharref^{b,*}, Rinaldo Poli^{a,d}^a CNRS, Laboratoire de chimie de coordination (LCC), Université de Toulouse, UPS, INPT, 205, route de Narbonne, 31077 Toulouse, France^b Laboratoire de chimie biomoléculaire, substances naturelles et réactivité, Unité associée au CNRST (URAC16), Université Cadi-Ayyad, Faculté des sciences Semlalia, BP 2390, boulevard My Abdellah, 40000 Marrakech, Morocco^c Université de Toulouse, Institut universitaire de technologie Paul-Sabatier, département de chimie, avenue Georges-Pompidou, CS 20258, 81104 Castres cedex, France^d Institut universitaire de France, 103, boulevard Saint-Michel, 75005 Paris, France

ARTICLE INFO

Article history:

Received 2 September 2013

Accepted after revision 28 January 2014

Available online 12 March 2014

Keywords:

Homogeneous catalysis

Tridentate ligands

Molybdenum

Natural products

Epoxidation

Green chemistry

Terpenoids

Mots clés :

Catalyse homogène

Ligands tridentate

Molybdène

Produits naturels

Époxidation

Chimie verte

Terpénoïdes

ABSTRACT

Himachalenes, sesquiterpenes isolated from the essential oil of *Cedrus atlantica*, are abundant and relatively inexpensive natural molecules of high interest, of which classical chemical transformations have enlarged the application potential. Solvent-free epoxidation using aqueous TBHP as an oxidant and $[\text{MoO}_2(\text{SAP})]_2$ as a catalyst is performed herein for the first time with this family of natural compounds and with related halogenated derivatives.

© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Les himachalènes, sesquiterpènes isolés à partir de l'huile essentielle du cèdre de l'Atlas (*Cedrus atlantica*), sont des molécules naturelles abondantes et relativement peu coûteuses présentant des propriétés intéressantes et dont les transformations chimiques classiques augmentent les applications potentielles. L'époxydation sans solvant utilisant TBHP en solution aqueuse comme oxydant et $[\text{MoO}_2(\text{SAP})]_2$ comme catalyseur est présentée ici pour la première fois avec cette famille de composés naturels et certains de leurs dérivés halogénés.

© 2014 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

1. Introduction

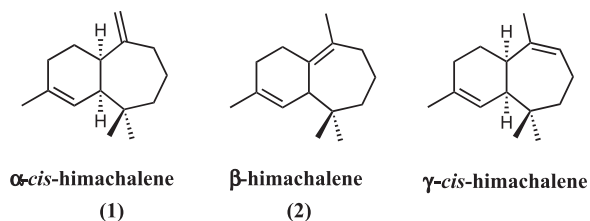
Plants are important natural sources of organic molecules used in different sectors, such as the perfume industry

as fragrances, the food industry as additives, or the cosmetics and the pharmaceutical industries [1]. Essential oils from plants are complex mixtures of several organic molecules, containing terpenes as notable components. These molecules bear several biological properties (biocides, pesticides), making them interesting biosourced compounds for many applications [2]. However, chemical transformation is crucial to generate derivatives with novel properties and uses [3]. In order to valorize these natural compounds, some of us have long been involved in the study

* Corresponding authors. Université de Toulouse, Institut universitaire de technologie Paul-Sabatier, département de chimie, avenue Georges-Pompidou, CS 20258, 81104 Castres cedex, France.

E-mail addresses: dominique.agustin@iut-tlse3.fr (D. Agustin), benharref@uca.ma (A. Benharref).

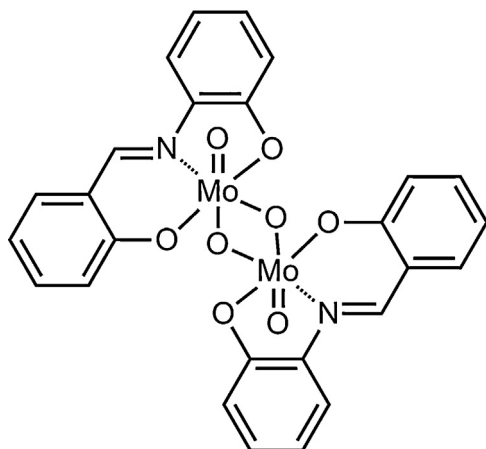
of the sesquiterpenes called “himachalenes” (see Scheme 1), extracted from the essential oil of *Cedrus atlantica*, an endemic tree in Morocco [4]. Himachalenes have been a



Scheme 1. Different himachalene isomers.

topic of investigation for several years. While research has been devoted to their total synthesis [5], other studies have revealed the versatility of natural himachalenes to different types of transformations (especially exploiting the selective reactivity of the double bonds) through reactions in organic solvents, such as Ru-catalysed aerobic epoxidation [6], diol formation using KMnO_4 [7] or epoxidation through *m*-CPBA [8] as well as formal dihalocarbene addition or halogen addition [7], these transformations leading to mono-olefinic compounds. From the formed epoxides, Lewis acid catalysed rearrangements have recently been described [9].

Himachalenes and their halogenated derivatives were epoxidized using the classical organic peroxide *m*-CPBA as an epoxidating agent in organic solvents, often chlorinated ones. With the increasing demand for cleaner and safer processes, the epoxidation of himachalenes and their derivatives should be revisited and hopefully lead to efficient and “greener” transformations. We are currently interested in solvent-free epoxidations and have reported efficient protocols for the epoxidation of cyclooctene using molybdenum- [10,11] and vanadium- [12] based catalysts, as well as polyoxometalates [13]. We present herein the results of the epoxidation reaction of the himachalenes using the solvent-free catalysed method using aqueous TBHP as an oxidant and $[\text{MoO}_2(\text{SAP})]_2$ (SAP = salicylidene-neaminophenolato) (Scheme 2) as a catalyst.



Scheme 2. $[\text{MoO}_2(\text{SAP})]_2$ catalyst.

2. Results and discussion

2.1. Himachalenes and chlorinated derivatives

The “raw” essential oil studied herein was extracted from the grinded wood of Atlantic Cedar (see Experimental part for details). This essential oil contains a high quantity (around 70% wt of the total oil) of the three himachalene isomers, called α -cis (1)-, β - (2) and γ -cis-himachalene, the isomerism depending on the position of the olefinic function of the 7-membered cycle (Scheme 1). The β -himachalene is the most abundant isomer in the mixture followed by the α -cis and a minor quantity of the γ -cis. The present work is focused on the study of the two main compounds 1 and 2.

Two methods were employed to obtain halogenated mono-olefinic compounds from himachalenes. The first halogenated compound, 3-chlorohimachal-7,13-ene, (3, Scheme 3) is the product of formal hydrochlorination of α -cis-himachalene. Action of gaseous HCl on a himachalene mixture followed by recrystallization in hot methanol leads to 3 as a unique species containing an exocyclic double bond [14]. The advantage of this compound in comparison to the himachalenes 1 and 2 is the presence of a unique double bond available for functionalization. The structure of this compound was elucidated by X-ray crystallography and ^{13}C NMR [15].

The second investigated halogenated himachalene derivative, (1*S*,3*R*,8*R*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo[6,4,0,0^{1,3}]-dodec-9-ene (4, Scheme 4), corresponds to the formal addition of a dichlorocarbene to the tetrasubstituted double bond of the β -himachalene (2), using *in situ* dichlorocarbene generation from chloroform and NaOH in the presence of an ammonium salt [16]. This compound was characterized by different methods, including single-crystal X-ray diffraction [17] and ^{13}C NMR [16].

2.2. Epoxidations

It has to be noticed that a few himachalene epoxides have already been identified as minor components of the essential oils [18]. However, the low natural quantity has stimulated investigations to find efficient synthetic epoxidation methods from the more abundant himachalenes using simple organic reactions (*m*-CPBA in chloroform or dichloromethane). According to the accepted mechanism of the epoxidation reaction [19,20], the reactivity is related to the electron density of the olefin double bond, leading to the reactivity trend shown in Scheme 5. The reactivity is also related to the electrophilic character of the oxygen atom transferred from the oxidant, hence *meta*-chloroperbenzoic acid (*m*-CPBA) is typically chosen as oxidizing agent [21].

All reactions using *m*-CPBA need the use of organic solvents. In the quest of greener reaction conditions, the recently introduced solvent-free method using $[\text{MoO}_2(\text{SAP})]_2$ as a catalyst was tested herein [12]. The advantages of this catalytic method are the use of a small quantity of catalyst (1% Mo vs substrate), a smoother oxidant (TBHP in water), and no added organic solvent.

Download English Version:

<https://daneshyari.com/en/article/170545>

Download Persian Version:

<https://daneshyari.com/article/170545>

[Daneshyari.com](https://daneshyari.com)