



Editor's Choice paper

Epoxidation of α -pinene catalyzed by methyltrioxorhenium(VII): Influence of additives, oxidants and solvents

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ARTICLE INFO

Article history:

Received 30 January 2011

Received in revised form 21 March 2011

Accepted 21 March 2011

Available online 31 March 2011

Keywords:

Homogeneous catalysis

Epoxidation

Methyltrioxorhenium

Terpenes

Pinene oxide

ABSTRACT

The epoxidation of α -pinene employing methyltrioxorhenium as catalyst is examined. The influence of mono- and bidentate Lewis basic additives (e.g. ^tbutylpyridine, 4,4'-dimethyl-2,2'-bipyridine, and Schiff-bases) is investigated. Additionally the impact of the oxidant (H₂O₂ in water or urea–hydrogen peroxide (UHP)) on the catalytic performance is studied. The effect of the solvent is also examined in order to determine the optimal conditions for the epoxidation of α -pinene. The best and straightforwardly applicable result is obtained when a ratio α -pinene:MTO:^tbutylpyridine:UHP of 200:1:40:600 is applied at 0 °C in nitromethane. In this case, α -pinene oxide is formed with 95% yield after 3 h with a turnover frequency (TOF) of 610 h⁻¹.

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1. Introduction

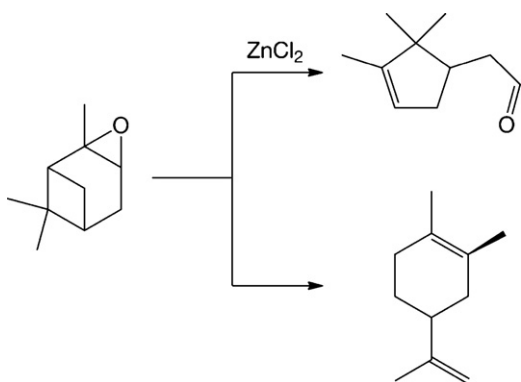
α -Pinene is a monoterpene which is an important ingredient of some flavoring plants such as mint, lavender and ginger. It is extracted from turpentine oil (350,000 t/year), which is a product of the paper pulp industry [1]. α -Pinene is particularly utilized as starting material in terpene chemistry to obtain flavors and fragrances. It is also an intermediary species in the synthesis of Taxol[®], an anticancer drug [2–4]. The epoxidized product of α -pinene, α -pinene oxide is used to synthesize campholeic aldehyde, an intermediate in the synthesis of the sandalwood fragrance [1]. α -Pinene oxide is additionally employed in the synthesis of trans-carveol, which is an important component for perfume bases and food flavor compositions (Scheme 1) [5].

The epoxidation of α -pinene in homogeneous phase has been studied in some detail in the past. Among the homogeneous catalysts applied for this reaction, methyltrioxorhenium [6–8] (MTO) is among the most widely used. However, in almost all cases the epoxidation suffers from either low conversion or low yield because of the formation of α -pinene diol as byproduct. Using the MTO–Lewis base adducts as catalysts does neither

prevent diol formation nor does it improve the epoxide yields [9,10]. A change of the oxidant to urea hydrogen peroxide (UHP) and addition of the base (+)-2-aminomethylpyrrolidine does not lead to a better selectivity according to the literature reports [11]. The reported conversion is still very low (<7%), when MTO is anchored to polymers such as poly(vinylpyridine) (PVP) or poly(vinylpyridine N-oxide) (OPVP) [12]. Although some reports claim that with MTO as catalyst, nearly quantitative yields of α -pinene oxide can be reached [13], we were unable to reproduce these results. Accordingly, the need for a straightforward, unproblematic procedure towards α -pinene oxide still remains. A wide range of other metals has been applied for the epoxidation of α -pinene. Molybdenum(VI) complexes have been studied for this reaction [14–20]. Co(III) supported material on hexagonal mesoporous silica (HMS) or Co supported by zeolite (NaCoY93) was investigated [21,22]. The synthesis of α -pinene oxide was also carried out with [Cu(pyridine)₂Cl₂] and the [CrO₃(2,2'-bipyridine)] as catalysts [23]. Lipase activity towards epoxidation of α -pinene has been studied [24,25]. [Ru(salophen)Cl-PSI] (PSI = polystyrene-bound imidazole) with NaIO₄ has also been employed for the formation of α -pinene oxide [26]. The epoxidation of α -pinene using (N,N-bis(salicylidene)ethylenediammine)Ti-salan complex is reported to lead to 85% epoxide yield after 7 h reaction time [27]. Based on these results, we set out to re-examine MTO as catalyst in the presence of Lewis basic additives, since such MTO based systems proved to be superior to other catalyst systems in many epoxidation reactions, provided optimal conditions were found.

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Scheme 1. Reaction of α -pinene oxide to campholeic aldehyde and to trans-carveol.

Additionally, MTO requires H_2O_2 as oxidant (Scheme 2), which has the advantage of being environmentally benign and cheap in comparison to other conventional oxidants used in epoxidations, e.g. meta-chloroperoxybenzoic acid (mCPBA).

Nevertheless, due to the high Lewis acidity of the Re(VII) center in presence of H_2O (the byproduct formed during the oxidation), ring opening of (sensitive) epoxides to diols occurs. It was shown that employing Lewis basic additives (Lewis base ligands) decreases the acidity of the rhenium center [8] and allows the synthesis of sensitive epoxides [9,28–33]. Particularly the use of pyridine and some of its derivatives, as well as Schiff base ligands leads in many cases to both good activity and high selectivity towards epoxidation of olefins (Scheme 2) [34–42].

In this work, we investigated the optimal and reproducible conditions for the epoxidation of α -pinene with MTO as catalyst. For this purpose, several mono- and bidentate base adducts were applied. Additionally, to eliminate potential problem sources, the effect of using different oxidants and reaction media, including ionic liquids, was examined.

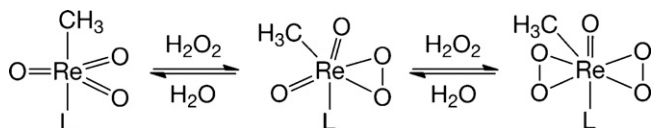
2. Experimental

2.1. Starting materials

Hydrogen peroxide was used 35% in water (Aldrich). (1R)-(+)- α -pinene was purchased from Aldrich. Urea Hydrogen Peroxide (UHP) contained 35 wt.% H_2O_2 (Acros organics). Methyltrioxorhenium and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF₆ were synthesized according to literature procedures [43–46].

2.2. Gas chromatography

Gas chromatography was performed using a DB23 column (30 m, 0.25 mm, 0.25 μm film thickness). The isothermal temperature profile is: 60 °C for the first 2 min, followed by a 10 °C/min temperature gradient to 105 °C for 10 min, then by 4 °C/min to 155 °C and finally 20 °C/min to 260 °C. The injector temperature was 320 °C. Chromatography grade helium was used as the carrier gas.



Scheme 2. Reaction of a MTO-Lewis base complex with H_2O_2 forming a mono- and bis(peroxo) complex, L = electron donor ligand [9,28–33].

2.3. Epoxidation of α -pinene in different solvents

2.3.1. Method A

MTO was dissolved in the solvent and the solution brought to the appropriate reaction temperature. The ligand, the two standards (mesitylene: 100 μL and ethylbenzene: 100 μL), and the oxidant (H_2O_2 35% or UHP) were added to the solution. α -Pinene was then added to the reaction. The different catalyst:ligand:oxidant ratios are given in Table 1. Samples were taken after 5 min, 10 min, 15 min, 30 min, 60 min, 90 min, 3 h, 5 h and 24 h. For each sample, 200 μL of the reaction mixture was taken and mixed with a catalytic amount of MnO_2 to decompose excess H_2O_2 . The mixture was then filtered through MgSO_4 in order to remove H_2O . CH_2Cl_2 (1.8 mL) was then added and the solution was analyzed by GC or stored in the freezer for several hours.

In this method, the samples are not stable, consequently, it is important to measure them directly in GC or to store them in the freezer. It is not possible to do several reaction in the same time. Consequently, a new method was found to stabilize the GC samples and allowed measurement over night.

2.3.2. Method B

MTO was dissolved in the solvent and the solution brought to the appropriate reaction temperature. The ligand, the two standards (mesitylene: 250 μL and ethylbenzene: 250 μL), and the oxidant (H_2O_2 35% or UHP) were added to the solution. α -Pinene was then added to the reaction. The different catalyst:ligand:oxidant ratios are given in Table 2. Samples were taken after 5 min, 30 min, 2 h, 5 h and 24 h. For each sample, 1.5 mL of the reaction mixture was taken and mixed with a catalytic amount of MnO_2 to decompose excess H_2O_2 . The mixture was then filtered and extracted 4 times with 1.5 mL of water to remove MTO. The organic layer was then dried over MgSO_4 and filtered. 0.18 mL (for H_2O_2) or 0.2 mL (for UHP) was taken from this solution and diluted with 1.3 mL of CH_2Cl_2 . The solution was then analyzed by GC.

2.4. Epoxidation of α -pinene in ionic liquids

MTO (0.024 mmol) and ^tbutylpyridine (5 equiv.) were dissolved in 1-butyl-3-methylimidazoliumhexafluorophosphate ([BMIM]PF₆) (0.2 mL). In a separate flask, mesitylene (100 μL), ethylbenzene (100 μL) and α -pinene (100 equiv.) were mixed together and a blank sample was taken from this solution. UHP or aqueous H_2O_2 (300 equiv.) was then added to the ionic liquid followed by the solution of α -pinene. The sampling time is the same as for conventional solvents. At defined times, 41 μL of the organic phase was poured in a vial containing MnO_2 in order to destroy excess oxidant, dried over MgSO_4 and filtered. 2 mL of CH_2Cl_2 were then added and the sample was analyzed by GC.

3. Results and discussion

3.1. Optimization of the conditions for the epoxidation of α -pinene

3.1.1. Lewis base concentration and temperature effects

In a previous work, optimal conditions for cyclooctene epoxidation with the system MTO/^tbutylpyridine/ H_2O_2 were determined [35]. The best result was obtained when a molar ratio cyclooctene:MTO:^tbutylpyridine: H_2O_2 of 100:1:5:300 in CH_2Cl_2 at 25 °C was applied.

The same conditions were used for the epoxidation of α -pinene. However, the formation of α -pinene diol was observed. From this observation it was deduced that α -pinene oxide appears to be more acid sensitive than cyclooctene oxide, being easily transformed to α -pinene diol in the presence of MTO and water (Scheme 3).

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