

Editor's Choice paper

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

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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

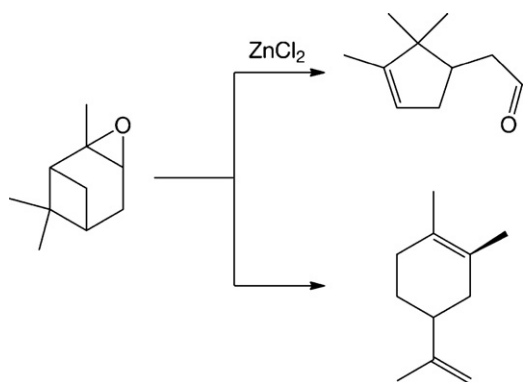
α -Pinene is a monoterpene which is an important ingredient of some flavoring plants such as mint, lavender and ginger. It is extracted from turpentine oil (350,000 t/year), which is a product of the paper pulp industry [1]. α -Pinene is particularly utilized as starting material in terpene chemistry 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.

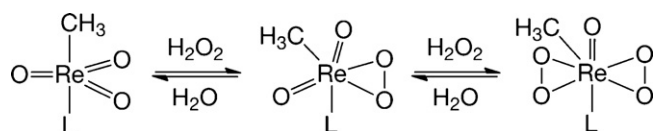
2. Experimental

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).

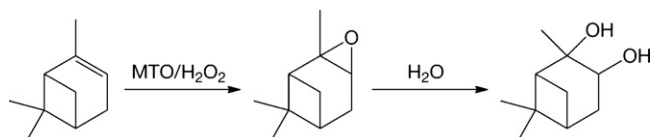
Table 1
Summary of the different ratios employed in the epoxidation of α -pinene.

Entry	α -Pinene ratio	MTO ratio (mmol)	^t butylpyridine ratio	H ₂ O ₂ ratio	CH ₂ Cl ₂ (mL)
1	100	1 (0.048)	5	300	2.3
2	100	1 (0.048)	10	300	2.3
3	100	1 (0.048)	20	300	2.3
4	100	1 (0.048)	20	150	1.2

Table 2
Summary of the different ratios employed in the epoxidation of α -pinene.

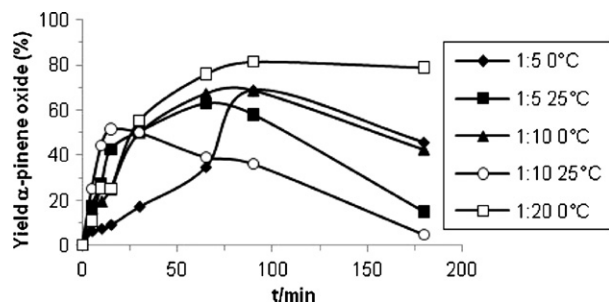
Entry	α -Pinene ratio	MTO ratio (mmol)	Ligand ^a ratio	H ₂ O ₂ ratio	Solvent ^b (mL)
1	100	1 (0.12)	20	150	7.6
2	100	0.5 (0.06)	10	150	7.6
3	100	0.1 (0.012)	2	150	7.6
4	100	1 (0.06)	20	150	7.8

Entry	α -Pinene ratio	MTO ratio (mmol)	Ligand ^a ratio	UHP ratio	Solvent ^b (mL)
5	100	1 (0.12)	20	150	8.4
6	100	0.5 (0.06)	20	150	8.4
7	100	1 (0.12)	20	300	8.4
8	100	0.5 (0.06)	20	300	8.4

^a ^tbutylpyridine, 4,4'-dimethyl-2,2'-bipyridine or two Schiff-bases.^b CH₂Cl₂, MeNO₂, CHCl₃ or THF.**Scheme 3.** Reaction from α -pinene to α -pinene diol in presence of MTO/H₂O₂ and water.

Accordingly, the Lewis acidity of the system has to be reduced by addition of an appropriate Lewis-base. Due to the beneficial effects of excess Lewis-base, originating from the weak Re–N interaction [47], an excess of ^tbutylpyridine was applied. To strengthen the base effect the reaction temperature was kept low.

All kinetic curves depicted in Fig. 1 show a feature which has not yet been described in detail in the previous reports on α -pinene epoxidation. The formation of α -pinene oxide is fast at the beginning of the reaction but after some time, the product yield not only becomes stagnant but decreases, reflecting the somewhat slower reaction to the respective diol becoming dominant. The formation of α -pinene diol is observed for all MTO:^tbutylpyridine ratios. However, a ratio of 1:20 at 0 °C leads to the highest yield of α -pinene oxide observed. Besides, the diol formation is less pronounced in comparison to the other cases. Thus, in the following reactions, the molar ratio between MTO and the ligands was kept at 1:20 and the reactions were performed at 0 °C.

**Fig. 1.** Kinetics of the α -pinene epoxidation with different molar ratios of MTO:^tbutylpyridine at 0 °C and 25 °C, ratio α -pinene:MTO:H₂O₂ is 100:1:300 in CH₂Cl₂.

3.1.2. Oxidant concentration effects

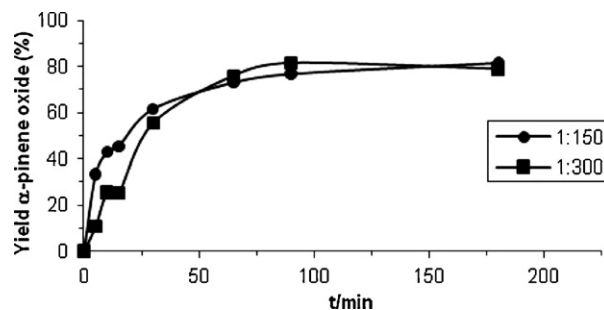
Another method to reduce the diol formation is to decrease the concentration of H₂O₂ in the reaction (see Fig. 2).

In the case of a molar MTO:H₂O₂ ratio of 1:300, the epoxide yield reaches a maximum (82%) after 1.5 h (conversion α -pinene = 96%) and then decreases, whereas in the case of a ratio of 1:150, the conversion is somewhat slower and reaches a maximum epoxide yield of 81% after 3 h (conversion α -pinene = 84%). Follow up diol formation is largely suppressed in the latter case. It is therefore more economical to use the lower concentration of hydrogen peroxide for the epoxidation of α -pinene.

3.1.3. Catalyst concentration effects

The concentration of MTO was decreased to establish the minimum concentration of catalyst needed to perform this reaction without activity loss. The ratio α -pinene:^tbutylpyridine:H₂O₂ used was 10:2:15.

Decreasing the concentration of MTO in the reaction from 1 mol% to 0.5 mol% leads to quite similar results (Fig. 3). The formation of α -pinene oxide is slightly higher after 2 h with 1 mol% (84% yield) than with 0.5 mol% (77% yield). Yet, the long-term activity (>1 d) of the catalyst is decreasing for concentrations below 1 mol%; the activity decreases more significantly when the concentration of MTO in the reaction is reduced to 0.1 mol%. To ensure both maximum yield and good activity the concentration of MTO was kept at a 1 mol% level for all following reactions. The poor activity at a catalyst concentration of 0.1 mol% may be due to several effects:

**Fig. 2.** Kinetics of the α -pinene epoxidation at 0 °C with a molar ratio of α -pinene:MTO:^tbutylpyridine 100:1:20 at different MTO:H₂O₂ ratios in CH₂Cl₂.

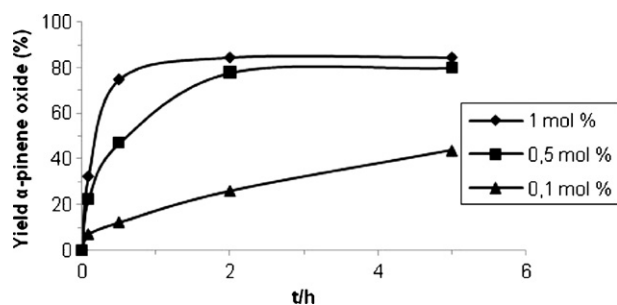


Fig. 3. Kinetics of the epoxidation of α -pinene with different MTO concentrations in CH_2Cl_2 .

first, MTO can decompose to methanol and perchlorate to a higher degree in the presence of large excess of oxidant [31]. Second, the Lewis base can also be oxidized in the presence of H_2O_2 [43,44,48]. Oxygen donor adducts of MTO, however, which are formed during this ligand oxidation process are less active than N-base adducts [43,44,48]. Third, impurities of oxidant and solvent have a stronger impact on catalyst deactivation when very low catalyst amounts are applied. In practical applications, however, a rigorous cleaning of the ingredients of the reaction mixture might be counterproductive with respect to reaction efficiency and costs.

3.2. Ligand-, oxidant-, and solvent-influence on the epoxidation of α -pinene

3.2.1. Ligand effects

The influence of a bidentate ligand (4,4'-dimethyl-2,2'-bipyridine), two different Schiff base ligands (2-[(E)-(phenylimino)methyl]phenol and 2,4-dichloro-6-[(2-chlorophenyl)imino]methyl]phenol) on the α -pinene oxide yield was examined (Scheme 4). The epoxidation of α -pinene was originally performed with a ratio substrate:MTO:ligand: H_2O_2 (100:1:20:150) in CH_2Cl_2 at 0°C . The results are summarized in Table 3.

The activity of the catalytic system MTO:^tbutylpyridine (1): H_2O_2 (TOF = 390 h^{-1}) is higher than the catalytic system MTO:4,4'-dimethyl-2,2'-bipyridine (2): H_2O_2 (TOF = 200 h^{-1}). Moreover, the formation of α -pinene diol is less pronounced when ^tbutylpyridine (1) is employed as Lewis basic additive, compared to 4,4'-dimethyl-2,2'-bipyridine (2). In contrast to pyridine-based Lewis bases, Schiff-base ligands 3 and 4 lead to a low selectivity in

Table 3
Comparison of the influence of ligands 1–4 on the epoxidation of α -pinene.

Ligand	Yield α -pinene oxide (time)	TOF (h^{-1})	Observation
1	85% (5 h)	390	Minor α -pinene diol formation
2	81% (5 h)	200	Minor α -pinene diol formation
3	6% (5 h)	20	α -pinene diol as main product
4	11% (5 h)	20	α -pinene diol as main product

the formation of α -pinene oxide (Table 3). In both examined cases, the main product is α -pinene diol. Consequently, ^tbutylpyridine (1) appears to be the best of the examined ligands as additive for the epoxidation of α -pinene. It was thus used for the following experiments.

3.2.2. Oxidant effect

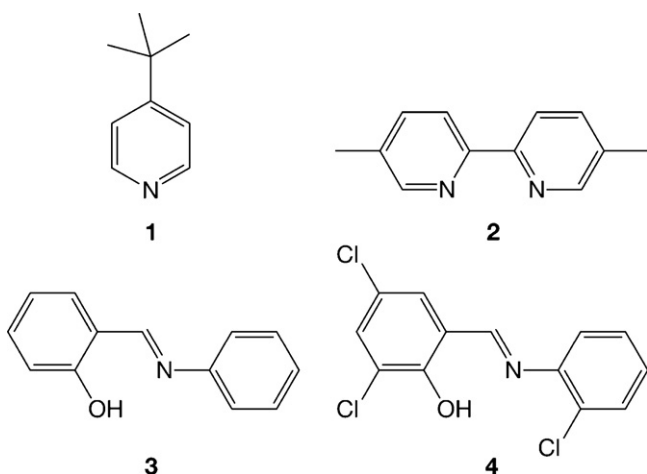
In all the previous experiments, α -pinene diol formation was observed. It was thus important to investigate other oxidants, which might prevent this unwanted follow-up reaction. Several reports describe the utilization of urea hydrogen peroxide (UHP) as an alternative oxidant to aqueous H_2O_2 in metal complex catalyzed olefin epoxidation reactions when acid sensitive epoxides are formed [49,50].

The catalytic reaction undertaken with the system MTO:UHP has approximately the same activity as the MTO: H_2O_2 system (see Fig. 4). However, the formation of α -pinene diol is only observed when H_2O_2 is used. UHP as oxidant does not lead to byproduct formation. However, the use of UHP can be problematic due to its solubility: it is barely soluble in most common organic solvents. Therefore, the real concentration of UHP in solution is hardly predictable, and the reaction cannot be described as really homogeneous. Based on these considerations, both UHP and H_2O_2 have certain advantages as oxidants for the epoxidation of α -pinene and will be used in the following experiments.

3.2.3. Solvent effects

Nitromethane, the ionic liquid ([BMIM]PF₆), CHCl_3 and THF were selected as solvents. Sharpless et al. demonstrated that the use of nitromethane and dichloromethane as solvent leads to similar efficiency in the epoxidation of cyclohexene [33]. Previous work [36,51–56] on epoxidation reactions in ionic liquids shows in many cases a yield improvement compared to organic solvents [52].

The epoxidation of α -pinene is favored when dichloromethane is used as solvent at 0°C . The use of other solvents such as nitromethane, chloroform or THF leads to lower formation of α -pinene oxide. However, the turnover frequencies measured for dichloromethane and nitromethane are close (see Table 4). In the case of the ionic liquid [BMIM]PF₆, the measurements proved to be problematic due to a significant amount of solid residue. Nevertheless, α -pinene diol appears to be the main prod-



Scheme 4. Lewis base ligands used in this study: 4-tert-butylpyridine (1), 4,4'-dimethyl-2,2'-bipyridine (2), 2-[(E)-(phenylimino)methyl]phenol (3) and 2,4-dichloro-6-[(2-chlorophenyl)imino]methyl]phenol (4).

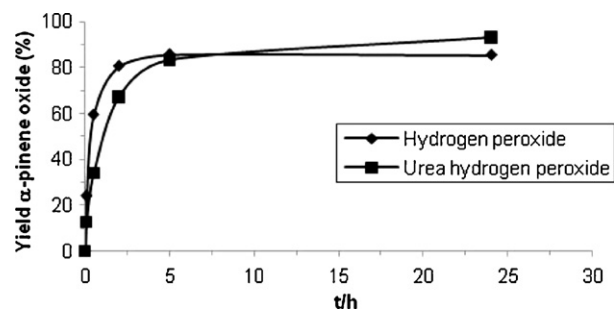


Fig. 4. Kinetics of the α -pinene epoxidation in CH_2Cl_2 at 0°C employing a ratio α -pinene:MTO:^tbutylpyridine:oxidant (100:1:20:150) with different oxidants.

Table 4
Comparison of the influence of H₂O₂ and UHP in different solvents.^a

Entry	Solvent	Yield % (TOF h ⁻¹)	
		H ₂ O ₂	UHP
1	CH ₂ Cl ₂	85 (400)	93 (150)
2	MeNO ₂	51 (330)	63 (290)
3	CHCl ₃	87 (100)	83 (100)
4	THF	47 (170)	29 (120)

^a Reaction condition: ratio α-pinene:MTO:^tbutylpyridine:oxidant (100:1:20:150) after 24 h reaction time.

Table 5
Optimization of α-pinene epoxidation employing UHP as oxidant.

Solvent	Ratio α-pinene:MTO: ^t butylpyridine:UHP ^a Yield % (TOF h ⁻¹)			
	100:1:20:150	200:1:40:300	100:1:20:300	200:1:40:600
CH ₂ Cl ₂	83 (150)	80 (450)	93 (200)	83 (210)
MeNO ₂	65 (290)	84 (420)	96 (270)	100 (610)

^a Samples taken after 5 h.

uct formed according to GC analysis. In the following experiments, dichloromethane and nitromethane were further used as solvent.

The conditions of α-pinene epoxidation were optimized for H₂O₂ as oxidant. So far, the best efficiency is obtained with either H₂O₂ or UHP as oxidant with a ratio of α-pinene:MTO:^tbutylpyridine:oxidant of 100:1:20:150. This condition leads to the formation of α-pinene oxide in 85% yield after 5 h. Further experiments were done to determine the optimal conditions of the epoxidation of α-pinene employing UHP as oxidant. For this purpose, the concentration of UHP was increased and the concentration of MTO was decreased.

As depicted in Table 5, increasing the concentration of UHP from 150 equiv. to 300 equiv. leads to higher formation of α-pinene oxide. Moreover, the formation of α-pinene diol is not observed in all these experiments. Decreasing the concentration of catalyst in the reaction leads to similar efficiency in nitromethane. From this set of experiments, the optimal condition for the epoxidation of α-pinene was found to be a ratio α-pinene:MTO:^tbutylpyridine:UHP of 100:0.5:20:300 in nitromethane at 0 °C. Formation of α-pinene oxide occurs with 95% yield after 3 h and quantitative yield after 5 h with a TOF of 610 h⁻¹.

4. Conclusion

MTO based catalytic systems were examined and optimized for practically applicable laboratory scale epoxidation of α-pinene. The major challenge of this reaction is the usually unwanted formation of diol that had not been sufficiently addressed in previous reports. Whereas the addition of ligands such as Schiff-bases or bipyridines does not suppress the formation of α-pinene diol, in the presence of ^tbutylpyridine the formed α-pinene oxide does not further react to the diol. However, the conditions leading to the best result involve the epoxidation of α-pinene can be achieved with either H₂O₂ or UHP as oxidant. However, the condition, which leads to the best result employed MTO as catalyst, ^tbutylpyridine as ligand and UHP as oxidant. It leads to the formation of α-pinene oxide in high yield (95% after 3 h) and to an acceptable TOF of 610 h⁻¹. No formation of α-pinene diol is observed in this case. This result is straightforwardly obtained when applying a α-pinene:MTO:^tbutylpyridine:UHP ratio of 200:1:40:600 in MeNO₂ at 0 °C.

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