Oxidation of α- and β-pinene catalyzed by Mn^{III}(Salen)Cl·H_2O

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The cationic complex Mn^{III}(Salen) is a very effective catalyst for the oxidation of both α- and β-pinene. The higher selectivity towards epoxide formation supports the rebound oxygen mechanism. A turnover of 40 was obtained for both compounds after 16 h of reaction with a molar ratio 1 : 0.01 : 1 (feedstock : catalyst : iodosobenzene) and conversions between 50 and 60% were observed. A very high selectivity (55%) was determined for epoxide formation from α-pinene. The good selectivity observed for myrtanal isomers (6.5 and 23.2%) from β-pinene is related to the prior formation of the 1,2-epoxides.

Keywords: α-pinene; β-pinene; Mn^{III}(Salen)Cl·H_2O; iodosobenzene; catalytic oxidation; cytochrome P-450

Cytochrome P-450 enzymes [1] play a significant role either in normal metabolism or in the metabolism of xenobiotic compounds [2]. These enzymes are responsible for the oxidation of a large range of inert organic compounds, thus playing an important role in detoxification. Several models for the mechanism of the action of these enzymes have been published [1–3]. To better understand the proposed mechanisms, models based on cytochrome $P\text{-}450_{CAM}$ have been studied extensively [4]. In these studies it was observed that this enzymatic complex is able to carry out hydroxylation of camphane and derivatives (monoterpenes) [4e]. Quite recently another enzymatic model, cytochrome $P\text{-}450_{terp}$ was described in the literature [5].

The accepted mechanism for hydroxylation with cytochrome P-450 involves the presence of a Fe^{IV}–$O^{\cdot}$ species, that can also be described as Fe^{V}=O [1–3]. Therefore, catalytic systems which are analogs of cytochrome P-450 should involve similar species.

Schiff bases' complexes of Cr(III) [6], Mn(III) [7], Fe(III) [8], and Co(II) [9] have been shown previously to be active catalysts for the oxidation of olefins. These systems can be considered analogs of cytochrome P-450, since their catalytic cycles involve oxometallic species (M=O) which are generated through a rebound mechanism analogous to M(porphyrins) [10].

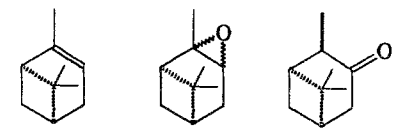
The use of a catalytic system based on Mn^{III}(Salen)Cl/iodosobenzene [#1] in the oxidation of limonene has been recently reported [11], and this system apparently involves Mn=O species via a rebound mechanism [7,10,12]. This paper reports on the application of this system to the oxidation of α- and β-pinenes.

α- and β-pinenes (Aldrich) were used as received. Reactions were conducted in CH_2Cl_2 under N_2 at room temperature. Molar ratios of α- or β-pinene : catalyst : oxidant from 1 : 0.01 : 1 to 1 : 0.05 : 1 were investigated in the present work. Reaction products were analyzed by HRGC, HRGC-MS, and HRGC-IR [13] (see appendix A.1 for details). Conversions and selectivities (appendix A.1) were based on calculated HRGC results by using the internal standard method.

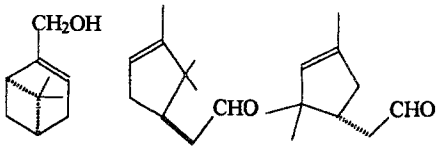
It was observed that in the absence of iodosobenzene no reaction occurred, while in the absence of the catalyst, keeping a 1 : 1 (α- or β-pinene : iodosobenzene) ratio, a 5% conversion of the feedstock took place.

Furthermore, for the oxidation of both α- and β-pinene, a turnover of 18 in 2 h was observed which reached 40 after 16 h of reaction keeping a feedstock : catalyst : iodosobenzene ratio of 1 : 0.01 : 1.

A conversion of 50–60% at 0.03–0.05 relative catalyst concentration was observed for α-pinene, yielding the corresponding epoxides (**1a** and **1b**), pinocamphone (**2**), and myrtenol (**3**), in addition to two other compounds (**4** and **5**) with the same M^+ ($m/z = 152$). (See appendix A.2 for details.)



α-pinene 1a / 1b 2



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[#1] For the preparation and characterization of the complex as well as titration of iodosobenzene see ref. [11].

The optimum yield for epoxide mixture (**1a** and **1b**) formation was over 20% (after 16 h of reaction), and the selectivities for their formation were around 55%. Yields in pinocamphone (**2**) and myrtenol (**3**) were very low (between 2 and 6%).

The infrared spectrum of **4** showed characteristic aldehyde absorptions (2709 and 1741 cm^{-1}), while **5** showed similar, although weaker, bands (2710 and 1739 cm^{-1}). The mass spectra of **4** and **5** were identical and based in their $M^+ = 152$, their formula were proposed to be $C_{10}H_{16}O$.

Upon bulb to bulb distillation, going to HRGC, a mixture of the epoxides (**1a** and **1b**), and **4** and **5**, and iodobenzene was detected. However, ^1H NMR analysis of this mixture showed only signals corresponding to the epoxides (**1a** and **1b**), in addition to aromatic signals corresponding to iodobenzene. These results indicate an isomerization of the epoxides (**1a** and **1b**) to **4** and **5** under our analytical conditions[#2].

Since under these conditions, i.e., over the column surface, a rearrangement of the epoxides into aldehydes, unsaturated alcohols and ketones is common [14], the presence of **4** and **5** is reasonable. Therefore, actual yields and selectivities corresponding to the epoxides **1a** and **1b** are even greater than those described above.

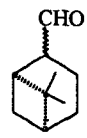
Since α-campholene aldehyde has been described [14] as a rearranged product from **1a** and/or **1b**, we compared its mass spectrum to that of **4** (and **5**) and we found them similar, although not coincident. Thus it is proposed that one of the rearranged products should be α-campholene aldehyde (**4**), while **5** must be an isomeric aldehyde.

For the oxidation of β-pinene, while keeping a molar ratio β-pinene : catalyst : iodosobenzene of 1 : 0.05 : 1, an optimal 55% conversion was achieved after 4 h of reaction, yielding myrtanal isomers (**6a** and **6b**) and 2,10-epoxipinane isomers (**7a** and **7b**) as main products. (See appendix A.2 for details.)

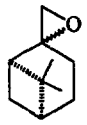
Maximum yields in myrtanal isomers were 6.5% (**6a**) and 23.2% (**6b**), while selectivities were 12 and 42%, respectively. Yields in epoxides (**7a** and **7b**) were very low (2–4%).

The ratio of the selectivities for myrtanal isomers (**6a** and **6b**) was observed to be constant (3.5) for the various molar ratios (β-pinene : catalyst : iodosobenzene) studied. These aldehydes (**6a** and **6b**) must be products originating from the epoxides (**7a** and **7b**), upon rearrangement [11]. Again, the real selectivity of the reaction toward epoxidation must be greater than shown here.

[#2]The determination of yields and selectivities for **1a** and **1b**, and **4** and **5** was a very difficult task due to the rearrangement of the epoxides into aldehydes and/or ketones. Very careful analyses, with several replications were needed. However, even under this protocol the bias is very high.



6a and 6b



7a and 7b

In conclusion, the present work deals with new and reliable processes for the oxidation of α- and β-pinene, yielding important compounds for the flavor and fragrance industry. The system Mn^{III}(Salen)Cl·H_2O/iodosobenzene, was shown to be very selective toward epoxide formation, supporting the oxygen rebound mechanism [7,10,12] analogously to cytochrome P-450 [15].

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Appendix

A.1. Experimental

Reaction procedure: In a typical procedure a convenient weight of catalyst was added to 20 ml of CH_2Cl_2 in a three-necked flask equipped with a tube for solid addition. While keeping the system under an inert atmosphere, 5 mmol of α- or β-pinene was added by using a syringe, followed by the addition of 5 mmol of iodosobenzene at once. After a determined reaction time, the reaction was worked up, an internal standard was added, the volume was made up to 25 ml with CH_2Cl_2, and samples analyzed.

Analysis: Silica capillary column (20 m × 0.32 mm) coated with SE-54 (0.3 μm); H_2 as carrier gas (2.5 ml/min); programmed temperature from 40 (6 min, α-pinene) or 50 (6 min, β-pinene) to 210°C (6°C/min). Oxidized monoterpenes were characterized and determined according to the MS and IR libraries. GC/MS analyses were performed in a HP 5987-A by using either electron impact or chemical ionization (isobutane). GC/IR analyses were performed in a HP 5965-A (4000 to 750 cm^{-1}).

$$\%\text{conversion} = 100(n_{\text{converted feedstock}}/n_{\text{feedstock initial}});$$

$$\%\text{yield} = 100(n_{\text{product}}/n_{\text{converted feedstock}});$$

$$\%\text{selectivity} = 100(\text{yield}/\text{conversion});$$

turnover = $n_{\text{converted feedstock}}/n_{\text{catalyst}}$.

A.2. Mass and IR spectra

MS (mass spectrum) of **1a** and **1b**, *m/z* (%): 108 (100), 93, 67, 91, 55, 41, 119, 152 ($M^{+\cdot}$); IR (cm^{-1}): 2996(s); 2931(s), 1380(w), 1210(w), 1011(w), 898(w).

MS of **2**, *m/z* (%): 83 (100), 55, 67, 95, 81, 109, 123, 69, 41, 152 ($M^{+\cdot}$); IR (cm^{-1}): 2941(s), 1707(s).

MS of **3**, *m/z* (%): 79 (100), 109, 59, 43, 93, 91, 119, 137, 152 ($M^{+\cdot}$); IR (cm^{-1}): 3609, 2962, 1464, 1384, 1127.

MS of **4** and **5**, *m/z* (%): 67 (100), 109, 83, 93, 41, 55, 95, 108, 119, 137, 152 ($M^{+\cdot}$); IR (cm^{-1}) of **4**: 3048, 2964, 2808, 2709, 1741; IR (cm^{-1}) of **5**: 2982, 2926, 2710, 1737.

MS of **6a** and **6b**, *m/z* (%): 79 (100), 67, 81, 69, 41, 82, 123, 109, 91, 83, 152 ($M^{+\cdot}$); IR (cm^{-1}) of **6a** and **6b**: 2929, 2802/2803, 2701, 1738, 1468/1469, 1383/1384.

MS of **7a** and **7b**, *m/z* (%): 69 (100), 67, 81, 82, 123, 83, 41, 79, 137, 109, 152 ($M^{+\cdot}$); IR (cm^{-1}) of **7a** and **7b**: 2994, 2926, 1445, 1376, 1053, 987, 799.

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