Oxidation of limonene catalyzed by $Mn^{III}(Salen)Cl{\cdot}H_2O$

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The cationic Mn^{III}(Salen) complex was proved to be an effective catalyst for the oxidation of limonene with iodosobenzene as terminal oxidant. For reactions conducted in CH_2Cl_2 at rt, with molar ratio of 1 : 0.05 : 1 (limonene : catalyst : iodosobenzene) limonene oxidation does occur with an optimal conversion of 60%. The major products according to HRGC-MS and HRGC-IR analyses were cis- and trans-1,2-epoxylimonene (30% and 16.7%, selectivity, respectively), the two diastereoisomers of 1-*p*-menthen-9-al (20% selectivity), and carvone (10% selectivity). A turnover of 60 was observed at 1 : 0.01 : 1 ratio. The higher selectivity toward epoxide formation supports the rebound oxygen mechanism.

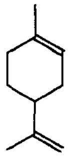
Keywords: limonene; $Mn^{III}(Salen)Cl{\cdot}H_2O$; iodosobenzene; catalytic oxidation

Schiff bases' complexes of Cr(III) [1], Mn(III) [2], Fe(III) [3], and Co(II) [4] have previously been shown to be active catalysts for the epoxidation of olefins. In these systems the active oxidizing species are $L_nM{=}O$, which are generated upon oxidation of the reduced species by suitable terminal oxidants. Groves et al. [5] have introduced the concept of rebound oxygen to explain mechanistically oxygen transfer from the terminal oxidant to the catalyst, and then to the olefin. Although allylic oxidation could also occur with these systems, these reactions are characteristic of radical processes that occur when the oxidizing species are in a lower oxidation state [6].

Because oxygen containing monoterpenes are very important flavor compounds and limonene is available in bulk quantities, we decided to investigate catalytic oxidation of this compound by using $Mn^{III}(Salen)Cl{\cdot}H_2O$ and iodosobenzene as a suitable terminal oxidant.

The complex was obtained as previously described [7]. It was characterized by elemental analysis and TGA, as well as by IR and UV–Visible spectra. Iodosobenzene was obtained by hydrolysis of the corresponding diacetate according to Saltzman and Sharefkin [8]. Upon titration by iodometry [9], it showed 98% active oxygen. Technical grade limonene 96% (orange essential oil) was used as feedstock as received. Reactions were conducted in CH_2Cl_2 under N_2 at room temperature (rt). Molar ratios limonene : catalyst : oxidant from 1 : 0.005 : 1 to 1 : 0.05 : 1 were investigated in the present work. Reaction products #1 were analyzed by HRGC #2, HRGC-MS, and HRGC-IR. Conversions and selectivities #3 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 (limonene : iodosobenzene) ratio, a 5% conversion of limonene took place. According to HRGC #2, HRGC-MS, and HRGC-IR results, limonene (**1**) oxidation yielded cis- and trans-1,2-epoxylimonene (**2**), carvone (**3**), and the two diastereoisomers of 1-*p*-menthen-9-al (**4**).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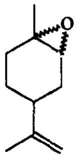
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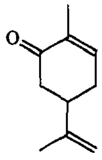
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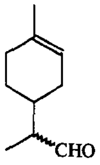
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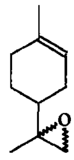
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Maximum turnover #2 was obtained after 25 h, reaching almost 60, with a 1 : 0.01 : 1 (limonene : catalyst : iodosobenzene) ratio. Increasing the relative concentration of catalyst from 0.005 to 0.05, while keeping limonene and iodosobenzene at 1 : 1 ratio, had a dramatic effect, so enhancing conversion up to 50–60%, at 0.03–0.05 relative catalyst concentration. The products' nature and proportion were little affected by varying either catalyst concentration or reaction time.

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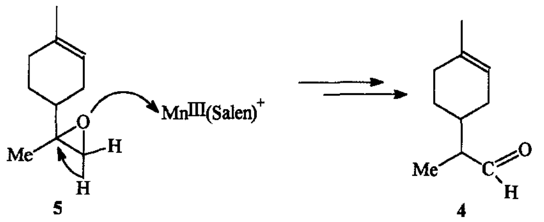
#1 In a typical procedure a convenient weight of catalyst was added to 20 ml of CH_2Cl_2 in a three-necked flask equipped with a tube for solid addition. While keeping the system under an inert atmosphere, 5 mmol of limonene was added by using a syringe followed by the addition of 5 mmol of iodosobenzene 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.

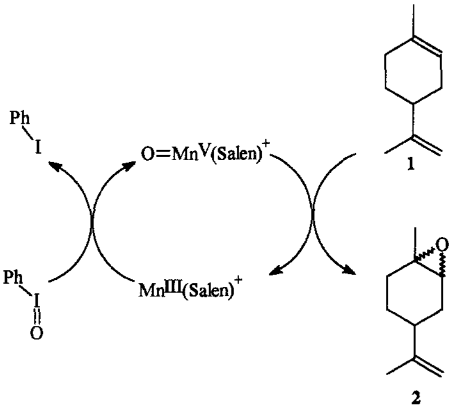
#2 $\%\text{conversion} = 100(n_{\text{converted feedstock}}/n_{\text{feedstock initial}})$; $\%\text{yield} = 100 \times (n_{\text{product}}/n_{\text{converted feedstock}})$; $\%\text{selectivity} = 100(\text{yield}/\text{conversion})$; $\text{turnover} = n_{\text{converted feedstock}}/n_{\text{catalyst}}$.

#3 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 70 to 200°C (3°C/min). Standard samples of carvone and 1,2-epoxylimonenes were used to determine these compounds. 1-*p*-menthen-9-al was tentatively determined according to the MS and IR libraries.

The following selectivities #3 were observed: 30 and 16.7% for cis- and trans-1,2-epoxylimonene (**2**), respectively, 18.4% for carvone (**3**), and 10% for either diastereoisomer of 1-*p*-menthen-9-al (**4**). A higher proportion of the cis-**2** was observed when Fe(porphyrin)Cl/PhIO [5b] or Mn(porphyrin)Cl/NaClO [10] was used. In these systems [5b,10] a 1 : 1 ratio for the diastereoisomers of 8,9-epoxylimonene (**5**) was observed. Since the same ratio was observed by us for the diastereoisomers of compound **4**, a rearrangement from **5** to **4** catalyzed by Mn^{III} can be suggested, since in CH_2Cl_2 Lewis acidity of Mn^{III} is increased:



To support this view it is worth pointing out that decomposition of epoxides in CH_2Cl_2 in a related system was previously described [2c]. The higher selectivity of this catalytic system toward epoxide formation suggests a rebound oxygen mechanism as previously proposed by Groves et al. [5] for related systems.



It is important to point out that the catalytic system described in the present work has a *perceived analogy* [11,12] with cytochrome P450 enzymatic system in which a rebound oxidation mechanism [5] is accepted.

The above findings, whenever applied on a preparative scale, would generate a new process for the production of oxygenated monoterpenes which has been the goal of different groups [13]. Since oxidation of this type of compounds generally occurs with poor reproducibility and very low yields and selectivities [4,12,13], the present work constitutes a new good entry for the production of oxygenated monoterpenes. The use of this catalytic system in other monoterpenes is under investigation.

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