

Autoxidation of limonene, α -pinene and β -pinene by dioxygen catalyzed by $\text{Co}(\text{OAc})_2/\text{bromide}$

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Abstract

It has been shown that NaBr addition to $\text{Co}(\text{OAc})_2$ increases conversions in autoxidations, by dioxygen, of limonene (1), α -pinene (2) and β -pinene (3). Best selectivities towards allylic oxygenated products were achieved with an optimum ratio $[\text{Co}(\text{OAc})_2]/[\text{NaBr}] = 1$, while keeping $[\text{Co}(\text{OAc})_2] = 0.15$ M. Using this system selectivities of 24.1, 11.4, 14.8 and 20.6% were obtained, respectively for carvone (4), *trans*-carveol (7a), *trans*- and *cis*-carvoyl acetate (9a and 9b) and 4-acetoxy-*p*-mentha-1,8-diene (13) from limonene (1). Autoxidation of α -pinene (2) showed selectivities of 10.2, 19.5 and 29.5% for myrtanal (6), verbenone (5) and *trans*-verbenyl acetate (17a), respectively. Very good selectivities, 19 and 15.4%, were observed for terpinyl acetate (27) and myrtanal (6) from autoxidation of β -pinene (3). Substitution of Co(II) by Mn(II) up to 30% M had no effect on conversions. However, this substitution (20–30% M) shifted selectivity significantly towards alcohols and acetates, yielding selectivities of 20 and 18% for *trans*-carveol (7a) and *trans*- and *cis*-carvoyl acetate (9a and 9b) from limonene (1); 48% for verbenyl acetate (17a) from α -pinene (2) and 16–18% for *trans*-pinocarveol (16) from β -pinene (3). It was concluded that, in this case, Mn(II) exercises a selectivity tuning effect.

Keywords: Limonene; α -Pinene; β -Pinene; Autoxidation; Co(II); Mn(II); NaBr; Catalysis; Dioxygen

1. Introduction

The metal bromide autoxidation of hydrocarbons, dubbed the AMOCO MC method, is now a fully established method for industrial oxidation of alkyl substituted aromatic hydrocarbons. The commercial importance of *p*-xylene oxidation to terephthalic acid by using Co/Mn/Br is outstanding; all commercial plants currently being built use this catalytic system [1]. However,

its use for allylic oxidation is much more limited [2–4], although some applications in the oxidation of ethylene [5] have been described.

Olefins are very useful intermediates for the chemical industry. These compounds can undergo either allylic oxidations or epoxidation reactions. Allylic oxidation is a process involving free radicals and this process is more likely to occur when the oxidizing metallic species is an intermediate in a low oxidation state [6]. Conversely, epoxide formation is normally related to the use of oxometallic species like $\text{O} = \text{Ru}^{\text{VIII}}$, $\text{O} = \text{Cr}^{\text{V}}$ or VI , $\text{O} = \text{Mn}^{\text{V}}$, among oth-

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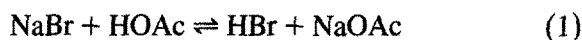
ers [7]. However, both *in vivo* and *in vitro*, both reactions have been shown to be competitive. Therefore, the occurrence of either the former or the latter mechanism is related not only to the nature of the metallic species and its degree of oxidation, but also to the nature of the olefin used and of the relative stability of the allylic radical formed [8].

Autoxidation studies on aldehydes and unsaturated hydrocarbons catalysed by $\text{Co}(\text{OAc})_2$ have established the fact that the catalyst activity is based on Co^{III} , which is formed during oxidation [9]. Other studies have proposed that $\text{Co}(\text{III})$ interacts with the double bond forming a very reactive radical-cation [10,11].

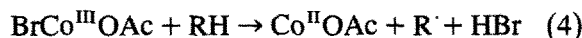
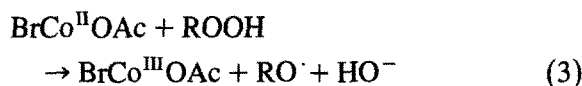
Oxidation of aromatic hydrocarbons by dioxygen, catalysed by cobalt salts has been studied extensively [1,12–19]. Blanchard [12] has observed that by using very pure starting materials, in the absence of free radical initiators, there is no reaction between cumene, dioxygen and Co^{II} , in acetic acid. When these oxidations occur, in the absence of free radical initiators, the initiation step probably results either from the presence of impurities, capable of initiating the process, or from the reaction between metallic ions and hydroperoxides (these hydroperoxides being generated upon thermal reaction between dioxygen and aromatic hydrocarbons).

Brill [13] has developed a process for terephthalic acid production via oxidation of *p*-xylene, in acetic acid, by using $\text{Co}(\text{OAc})_2$ and dioxygen and using methyl ethyl ketone as activator, with reported yields of over 90%. Takaya, Koga and Hara [14] have reported that under the same conditions described by Brill [13], but using NH_4Br and $\text{Cl}_2\text{C}=\text{CCl}_2$ as activators, yields were 85% (air) and 95% (dioxygen). Furthermore, under these conditions, reported reaction times were one-fourth of those reported by Brill [13]. Hay and Blanchard [15] have verified that systems containing $\text{Co}(\text{II})$ and $\text{Co}(\text{III})$ ions, dioxygen and bromide, in acetic acid, were effective catalytic systems for the oxidation of alkylaromatic hydrocarbons. They have sug-

gested also that the active species is $\text{AcOCo}^{\text{II}}\text{Br}$, formed according to Eqs. (1) and (2).



Since in acetic acid HBr is a weaker acid than it is in water [20], it exists in the unionized form (Eq. (1)), thus the effective concentration of this acid favors $\text{AcOCo}^{\text{II}}\text{Br}$ formation (Eq. (2)). Therefore, when $\text{Co}(\text{II})$ is oxidized to $\text{Co}(\text{III})$, a very reactive species is formed (Eq. (3)) and this species is able to abstract a hydrogen from the hydrocarbon, generating a free radical (Eq. (4)).



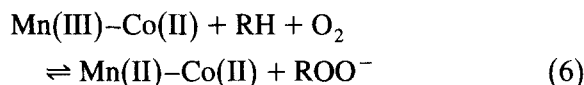
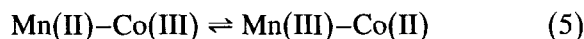
Partenheimer [1,21] has reported a detailed study on the reactivity of systems constituted of metallic acetates, dioxygen and acetic acid and concluded that $\text{Co}(\text{OAc})_2$ was effectively active as a catalyst in this kind of reaction. Furthermore, the addition of NaBr to these systems was effective only with $\text{Co}(\text{OAc})_2$ and $\text{Mn}(\text{OAc})_2$.

Partenheimer [22] also has characterized the reaction between $\text{Co}(\text{OAc})_2$ and dioxygen in acetic acid in the absence of feedstock and determined the presence of $\text{Co}^{\text{III}}(\text{OAc})_3$. The performance of this system in the presence of phenol, which completely suppressed the reaction, supported the proposed free radical mechanism, because phenol is a known free radical quencher.

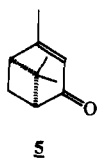
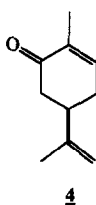
Hanotier and Hanotier-Bridoux [23] have claimed that cobalt(II) acetate “is not a well defined species” and, therefore, the catalytic activity of these systems should be related to the presence of dimeric species like $\text{Co}^{\text{III}}-\text{Co}^{\text{III}}$, while the dimeric species $\text{Co}^{\text{III}}-\text{Co}^{\text{II}}$ should be less active as an oxidizing species and the role of the promoters would be the production of peroxides capable of regenerating $\text{Co}^{\text{III}}-\text{Co}^{\text{III}}$.

Catalytic systems containing $(\text{Mn}(\text{II}) \text{ and } \text{Mn}(\text{III}))/(\text{Co}(\text{II}) \text{ and } \text{Co}(\text{III}))$ have been fre-

quently used in the oxidation of alkylaromatic hydrocarbons. Ravens [16] has reported that the substitution of 20% of $\text{Co}(\text{OAc})_2$ by $\text{Mn}(\text{OAc})_2$ was capable of enhancing the reaction rate by 5. According to Partenheimer [1,21], the role of $\text{Mn}(\text{II})$ was to decrease the effective $[\text{Co}^{\text{III}}]$, thus inhibiting the decomposition of acetic acid. In addition, it has been suggested that the formation and consumption of $\text{Mn}(\text{III})$ would occur via a dimeric species, according to Eqs. (5) and (6).



Monoterpenes are very important compounds with many uses. Among these compounds, limonene (1), α -pinene (2) and β -pinene (3), which are the most abundant, are suitable feedstocks for production of, for instance, carvone (4), verbenone (5) and myrtenal (6), respectively, which are important compounds for the flavor and fragrance industry. Due to this importance several groups have been working on the oxidation of monoterpenes [24,26–37].



Therefore, due to the economic importance of oxidized monoterpenes, associated with the fact that in many cases catalytic systems containing $\text{Co}(\text{II})/\text{Co}(\text{III})$ proved to be very selective [12–19,21–38] for benzylic oxidation and used less extensively on the oxidation of olefins [2–5], it was decided to study the autoxidation of limonene (1), α -pinene (2) and β -pinene (3), by dioxygen, catalysed by $\text{Co}(\text{II})/\text{Co}(\text{III})$, in glacial acetic acid¹. Furthermore, a very high selectivity has been claimed [39] in using of this kind of system on the allylic oxidation of a related compound, α -ionone, which is a very reactive norcarotenoid.

2. Experimental

High resolution gas chromatography (HRGC) analyses were performed in a HP 5890, by using a 25 m capillary column (0.30 mm ID) coated with SE 54 (0.3 μm) at 2.5 ml/min, H_2 as carrier gas, 220°C (injector temperature), 260°C (detector temperature), 50°C (oven initial temperature), 220°C (oven final temperature), 5°C/min (oven heating rate) and 1:20 (split ratio).

High resolution gas chromatography–mass spectrometry (HRGC–MS) analyses were performed under the same chromatographic conditions by using a HP 5985-A GC-MS system, 40–400 u, electron impact (70 eV), chemical ionization (*iso*-butane), under 200°C (ion source temperature).

High resolution gas chromatography–infra red spectrometry (HRGC–IR) analyses were performed in a HP 5965 A, from 4000 to 750 cm^{-1} , with He as carrier gas (15 psi).

2.1. Typical procedure

In a two-necked flask, equipped with a coiled condenser and two septa pierced with needles

¹ Glacial acetic acid was used, although it is very well known that these oxidations liberate water and that the level of water limits the reactivity of the catalytic system.

(inlet and outlet for dioxygen), containing 20 ml (total volume) of a 0.05, 0.10 or 0.15 M AcOH solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and the suitable $[\text{NaBr}]$, under stirring, kept at 50°C , dioxygen was bubbled (30 mL/min) for 15 min. After this period, without interrupting dioxygen flow, 1.36 g (10 mmol) of limonene (**1**), α -pinene (**2**) or β -pinene (**3**) was added via syringe. After the desired reaction time (6 or 24 h) pH was adjusted to 6.0–6.5 with 2 M NaOH. This solution was then submitted to a continuous extraction with AcOEt during 12 h and concentrated under vacuum. To this concentrated solution was added 392 mg (2.5 mmol) of PhBr (internal standard), the volume was made up to 25 ml and this solution was analysed by GC.

- Carvone (**4**): Mass spectrum (MS)/electron impact (EI), m/z: 82(100%); 54; 93; 108; 41; 107; 53; 79; 91; 150(M^+). IR, cm^{-1} : 3087; 2935; 1696; 1445; 1370; 898.

- Verbenone (**5**): MS/EI, m/z: 107(100%); 135; 91; 80; 79; 77; 41; 105; 108; 150(M^+). IR, cm^{-1} : 3052; 2941; 1708; 1621.

- Myrtenal (**6**): MS/EI, m/z: 79; 107; 91; 77; 108; 106; 105; 41; 135; 150(M^+). IR, cm^{-1} : 2996; 2932; 2800; 2711; 1704; 1623.

- *trans*-Carveol (**7a**): MS, m/z: 109(100%); 84; 55; 41; 91; 83; 119; 123; 137; 152(M^+). IR, cm^{-1} : 3643; 2928; 1644; 1447; 1380; 1046; 957; 895.

- Perilaldehyde (**8**): MS/EI, m/z: 67(100%); 79; 107; 91; 93; 53; 122; 135; 150(M^+). IR, cm^{-1} : 3087; 2942; 2804; 2715; 1710; 1645; 1444; 1381; 896.

- *trans*- and/or *cis*-Carvoyl acetate (**9a** and/or **9b**): MS/EI, m/z: 109(100%); 119; 84; 152; 43; 134; 92; 93; 94; 107. IR, cm^{-1} : 3082; 2943; 1754; 1373; 1230; 1020.

- 1,2-Diacetoxy-*p*-menth-8-ene (**10**): MS/EI, m/z: 71(100%); 43; 108; 109; 152; 67; 69; 93; 82; 137. IR, cm^{-1} : 2949; 2878; 1755; 1373; 1236.

- 1-Hydroxy-2-bromo-*p*-menth-8-ene (**11**): MS/EI, m/z: 71(100); 135; 93; 108; 43; 67; 55; 68; 214(M^+); 216($\text{M}^+ + 2$). IR, cm^{-1} : 3640; 3084; 2947; 1644; 1448; 1382; 1180; 895.

- 2-Acetoxy-*p*-menth-1,8-diene (**12**): MS/EI, m/z: 109(100%); 43; 152; 137; 71; 93; 67; 81; 55; 41. MS/Chemical Ionization (CI): 135(100%); 135; 154; 195($\text{M}^+ + 1$). IR, cm^{-1} : 3082; 2944; 1762; 1644; 1449; 1376; 1239; 1031.

- 4-Acetoxy-*p*-menth-1,8-diene (**13**): MS/EI, m/z: 43(100%); 134; 119; 95; 67; 71; 105; 137; 79; 194(M^+). IR, cm^{-1} : 3084; 2946; 1753; 1644; 1448; 1372; 1248; 1174; 1039.

- *trans*-Pinocarveol (**16**): MS/EI, m/z: 92(100%); 91; 55; 70; 83; 41; 81; 79; 119; 109. IR, cm^{-1} : 3638; 3037; 2987; 2931; 1089; 1007.

- *trans* and/or *cis*-Verbenyl acetate (**17a** and/or **17b**): MS/EI, m/z: 119(100%); 43; 109; 91; 93; 77; 134; 41; 55; 71. IR, cm^{-1} : 2999; 2937; 1756; 1375; 1236; 1019.

- 3-Acetoxy-2,6,6-trimethylbicyclo[3.1.1]hepta-2-ene (**18**): MS/EI, m/z: 43(100%); 108; 150; 107; 109; 105; 135; 59; 95; 82. IR, cm^{-1} : 2937; 1755; 1374; 1230; 1016.

- Pinocamphone (**22**): MS/EI, m/z: 83(100%); 55; 67; 95; 81; 109; 123; 69; 41; 152 (M^+). IR, cm^{-1} : 2937; 1737; 1467; 1197.

- Pinocarvone (**23**): MS/EI, m/z: 81(100%); 53; 108; 107; 79; 135; 41; 77; 69; 150 (M^+). IR, cm^{-1} : 2990; 2935; 1723; 1631; 1467; 936.

- Fenchyl Acetate (**24**): MS/EI, m/z: 81(100%); 43; 80; 93; 121; 36; 67; 69; 79; 107. IR, cm^{-1} : 2962; 2885; 1755; 1468; 1376; 1242; 1049.

- Bornyl Bromide (**25**): MS/EI, m/z: 137(100%); 81; 95; 69; 41; 67; 91; 93; 136; 201; 203. IR, cm^{-1} : 2961; 2891; 1466; 1385; 1248; 788.

- Bornyl Acetate (**26**): MS/EI, m/z: 95(100%); 43; 93; 121; 136; 55; 67; 79; 108; 109. IR, cm^{-1} : 2962; 2890; 1756; 1372; 1242; 1034.

- α -Terpinyl Acetate (**27**): MS/EI, m/z: 121(100%); 93; 43; 136; 67; 79; 91; 77; 59; 107. IR, cm^{-1} : 2936; 1751; 1372; 1250; 1134; 1017.

- 2-Acetoxy-6-bromo-1,5,5-trimethyl-

norbornane (**28**): MS/EI, m/z : 83(100%); 135; 139; 55; 93; 177; 179; 41; 69; 79. IR, cm^{-1} : 2961; 1766; 1375; 1376; 1228; 1032; 929.

3. Results and discussion

Since the selected monoterpenes are known to be very reactive, in order to carry out this study mild conditions were chosen, according to the literature [14,15,39]. Therefore, a temperature of 50°C, a dioxygen flow of 30 ml/min, reaction times of 6 h (in the presence of NaBr) and 24 h (in the absence of NaBr) and 10 to 30% relative molar concentrations of catalyst/feedstock were used in the present work.

3.1. Effect of [NaBr] on conversions

In the absence of $\text{Co}(\text{OAc})_2$, no reaction was observed between dioxygen and the feedstocks. In the presence of $\text{Co}(\text{OAc})_2$, with a 24 h reaction time, a 30–40% conversion² was noticed, which was not dependent on the initial [Co(II)]. However, product selectivity toward any specific oxygenated product was less than 5%. The initial intense pink solution of $\text{Co}(\text{OAc})_2$ turned to red/brownish and slowly, to dark green, thus showing the presence of Co(III). Addition of bromide ions increased conversions considerably, with a 6 h reaction time and these were dependent on the initial [Co(II)]. Table 1 shows the effect of [Co(II)] on the feedstock conversion, while keeping $[\text{NaBr}]/[\text{Co}(\text{OAc})_2] = 1$. Feedstock conversion was dramatically dependent on the $[\text{NaBr}]:[\text{Co}(\text{OAc})_2]$ ratio. Thus, maintaining $[\text{Co}(\text{OAc})_2] = 0.15 \text{ M}$ and $[\text{NaBr}]/[\text{Co}(\text{OAc})_2] = 4$, feedstock conversion was 100% (Table 2). Therefore, these results support the reported

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

Table 1
Effect of $[\text{Co}(\text{OAc})_2]$ on feedstock conversion^a

| $[\text{Co}(\text{OAc})_2]$ (M) | % Conversion | | |
|---------------------------------|--------------|----------------------|---------------------|
| | limonene (1) | α -pinene (2) | β -pinene (3) |
| 0.05 | 50 | 66 | 53 |
| 0.10 | 60 | 76 | 65 |
| 0.15 | 65 | 80 | 68 |

^a $[\text{NaBr}]/[\text{Co}(\text{OAc})_2] = 1$.

catalytic effect of bromide ions in this kind of reaction [13,15,21].

According to Table 2, for $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ ratios greater than 2, very high conversions were observed. However, these very high conversions were accompanied by very low selectivities. At these high ratios, reaction products originating from Br_2 addition to double bonds were observed. The presence of Br_2 can be related [23] to a high concentration of Br^{\cdot} , possibly originating from $\text{Co}(\text{OAc})_3$ reduction by Br^- [22].

3.1.1. Autoxidation of limonene (1)

High resolution gas chromatography–mass spectrometry (HRGC–MS) and high resolution gas chromatography–infra red (HRGC–IR) analyses showed the products of autoxidation of limonene to be carveol (**7a** and/or **7b**), carvone (**4**), perillaldehyde (**8**), carvonyl acetate (**9a** and **9b**), 1,2-diacetoxy-*p*-mentha-8-ene (**10**), 1-hydroxy-2-bromo-*p*-mentha-8-ene (**11**), 2-acetoxy-*p*-mentha-1,8-diene (**12**) and 4-acetoxy-*p*-

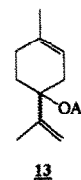
Table 2
Effect of $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ molar ratios on feedstock conversion^a

| $[\text{NaBr}]/[\text{Co}(\text{OAc})_2]$ | % Conversion | | |
|---|--------------|----------------------|---------------------|
| | limonene (1) | α -pinene (2) | β -pinene (3) |
| 0 | 30 | 40 | 37 |
| 0.5 | 60 | 76 | 63 |
| 1 | 65 | 80 | 68 |
| 2 | 79 | 89 | 82 |
| 3 | 98 | 100 | 99 |
| 4 | 100 | 100 | 100 |

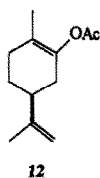
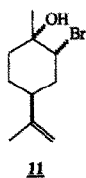
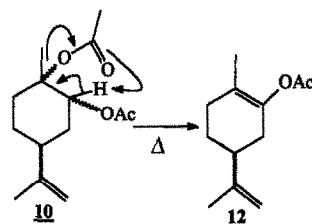
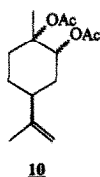
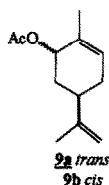
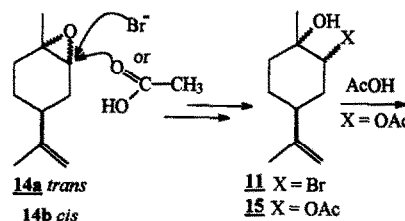
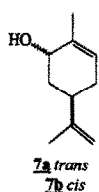
^a $[\text{Co}(\text{OAc})_2] = 0.15 \text{ M}$.

mentha-1,8-diene (**13**), in chromatographic elution order, respectively.

Reaction products **10**, **11** and **12** probably originated from epoxide **14a** or **14b** [40], which could be formed in the reaction medium. Compound **10** probably originated from **14a** or **14b**, via nucleophilic attack of AcOH to the epoxide ring, followed by esterification of the hydroxyl group with AcOH. Compound **11** probably originated from nucleophile attack of bromide ion to the epoxide ring, while **12** should form from **10**, upon dehydroacetoxylation.



The predominant allylic attack towards an endocyclic double bond shows its higher reactivity, probably related to its more favorable nucleophilicity.



In order to increase selectivity towards carvone-related products (**4**, **7a**, **7b**, **9a** and **9b**), various catalytic combinations were tested. The best results are shown in Table 3. The best compromise between $[\text{Co}(\text{OAc})_2]$ and molar ra-

Table 3
Effect of $[\text{Co}(\text{OAc})_2]$ and molar ratio $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ on the selectivity of autoxidation of limonene (**1**)

| Catalyst | | % Selectivity | | | |
|---------------------------------|---|---------------|-------------------------------|-------------------------------|-----------|
| $[\text{Co}(\text{OAc})_2]$ (M) | $[\text{Co}(\text{OAc})_2]/[\text{NaBr}]$ | 4 | 7a and 7b ^a | 9a and 9b ^b | 13 |
| 0.05 | 1:1 | 10.8 | 7.2 | 8.1 | 10.2 |
| 0.10 | 1:1 | 14.0 | 10.6 | 11.5 | 20.0 |
| 0.15 | 1:0.5 | 17.1 | 8.7 | 7.3 | 22.2 |
| 0.15 | 1:1 | 24.1 | 11.4 | 14.8 | 20.6 |
| 0.15 | 1:2 | 10.5 | 3.3 | 3.6 | 7.9 |

^a Co-elution studies, as well as IR and MS spectra indicated the formation of **7a**. However, retention times for **7a** and **7b** are so close and their spectra so similar, that the presence of **7b** could not be discarded.

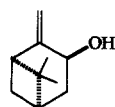
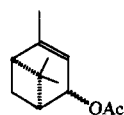
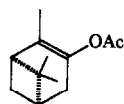
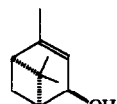
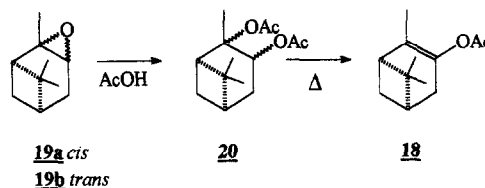
^b It was not possible to achieve a good chromatographic resolution for **9a** and **9b**. Therefore, the results shown in this table represent the total area of the isomeric mixture.

tios $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ to obtain the best selectivity toward carvone related products was achieved when $[\text{Co}(\text{OAc})_2] = [\text{NaBr}] = 0.15 \text{ M}$. The results disclosed here represent a new, highly selective, process towards carvone related products, with a selectivity closed to that described by Lohri [39] for the oxidation of α -ionone. Furthermore, while a highly selective process towards **13** has been described in the literature by using SeO_2 [41], lower selectivities were found for carvone-related products [38].

This high selectivity observed for limonene (**1**) autoxidation products, encouraged the use of the catalytic systems described above for the oxidation of α -pinene (**2**) and β -pinene (**3**). Furthermore, our yields and selectivities towards allylic oxidation products appeared to be better than those claimed by Hay [3] in the oxidation of cyclohexene.

3.1.2. Autoxidation of α -pinene (**2**)

Autoxidation of α -pinene (**2**) yielded *trans*-pinocarveol (**16**), verbenone (**5**), myrtenal (**6**), *trans*- and *cis*-verbenyl acetate (**17a** and **17b**) and 3-acetoxy-2,6,6-trimethyl[3.1.1]bicyclohepta-2-ene (**18**) [42].

**16****17a trans****17b cis****18****21****19a cis****19b trans****20****18**

Verbenone (**5**), myrtenal (**6**) and *trans*-verbenyl acetate (**17a**) were the main products of α -pinene (**2**) autoxidation. According to Table 4, the highest selectivity for these compounds was achieved under the same catalytic conditions where limonene (**1**) yielded carvone related products, thus showing that under these conditions a high selectivity towards allylic oxidation was obtained, although not suppressing epoxide formation. Furthermore, the higher selectivity towards allylic oxidation is explained considering that the pinane system is much more rigid than the menthane system and that in the pinane system a higher strain is expected during epoxide formation.

Kinetic resolution toward *trans*-verbenol (**21**) and *trans*-epoxide (**19b**) by using a racemic isomeric mixture of α -pinene was recently reported [43] to occur by using a chiral Fe(Porphyrin). Selective methods to epoxide formation and allylic oxidation starting from optically active α -pinene have previously been reported [33,43,44]. The selectivity showed in

Table 4
Effect of $[\text{Co}(\text{OAc})_2]$ and molar ratio $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ on the selectivity of autoxidation of α -pinene (**2**)^a

| Catalyst | | % Selectivity | | |
|---------------------------------|---|---------------|----------|-------------------------|
| $[\text{Co}(\text{OAc})_2]$ (M) | $[\text{Co}(\text{OAc})_2]/[\text{NaBr}]$ | 6 | 5 | 17b ^b |
| 0.05 | 1:1 | 5.7 | 10.9 | 17.0 |
| 0.10 | 1:1 | 8.9 | 17.2 | 26.6 |
| 0.15 | 1:0.5 | 3.8 | 15.7 | 24.8 |
| 0.15 | 1:1 | 10.2 | 19.5 | 29.5 |
| 0.15 | 1:2 | 2.5 | 7.8 | 21.8 |

^a The selectivities observed for **16** and **18** were too low to be considered here.

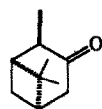
^b Although the presence of **17b** was not confirmed, this compound is expected to have a similar chromatographic behaviour to the **17a**, as well as similar IR and MS spectra.

In analogy to limonene (**1**) [40], formation of 3,4-epoxypinane (**19**) from α -pinene (**2**) should yield **20**, upon nucleophilic attack of AcOH on the epoxide ring. Dehydroacetoxylation of 3,4-diacetoxypinane (**20**) should then yield **18**.

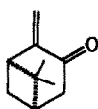
the present work is therefore comparable to those previously described [37]. Furthermore, starting from chiral α -pinene, as reported in the present work, represents an alternative entry to these compounds in holemic or scalemic form³, because although a ring rearrangement is expected to occur [44,45], racemization is not expected to occur in the pinane series. Since verbenone is considered to be a suitable precursor to taxol, a correct choice of the suitable α -pinene enantiomer, available in both chiral forms, should lead to a proper intermediate for an asymmetric synthesis of taxol [46].

3.1.3. Autoxidation of β -pinene (3)

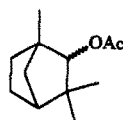
Autoxidation of β -pinene (3) catalysed by $[\text{Co}(\text{OAc})_2]/[\text{NaBr}]$ produced a great number of products from which pinocamphone (22), *trans*-pinocarveol (16), myrtenal (6), pinocarvone (23), fenchyl acetate (24), bornyl bromide (25), bornyl acetate (26), α -terpinyl acetate (27), and 2-acetoxy-6-bromo-1,5,5-trimethylnorbornane (28), could be identified according to their MS and IR spectra.



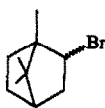
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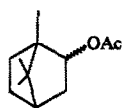
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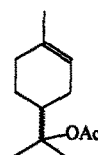
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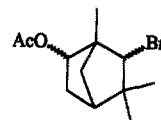
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27



28

Compounds 6, 16 and 23 resulted from allylic oxidation of β -pinene (3), while 22 must originate from epoxides 19a and/or 19b. These epoxides (19a and/or 19b) would be formed from α -pinene (2), which in turn could either be originated from β -pinene (3) or could be present in the reaction medium as a contaminant. Formation of 24, 25, 26, 27 and 28 resulted from the very well known pinane–bornane–fenchane skeleton rearrangement [47,48].

Autoxidation of β -pinene (3) led to products in low yields. Several catalytic systems were tested, without any noticeable effect on selectivity, by varying $[\text{Co}(\text{OAc})_2]$. Best results were obtained for myrtenal (6) and terpinyl acetate (27), by using $[\text{Co}(\text{OAc})_2] = [\text{NaBr}] = 0.15 \text{ M}$, as indicated in Table 5. Therefore, as seen in Table 5, a reasonably selective system was developed for oxidation of β -pinene (3). In addition, the selectivities disclosed in the present

Table 5

Effect of $[\text{Co}(\text{OAc})_2]$ and molar ratio $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ on the selectivity of autoxidation of β -Pinene (3)

| Catalyst | | % Selectivity | | | |
|---------------------------------|---|---------------|-----|-----|------|
| $[\text{Co}(\text{OAc})_2]$ (M) | $[\text{Co}(\text{OAc})_2]/[\text{NaBr}]$ | 6 | 16 | 23 | 27 |
| 0.05 | 1:1 | 12.5 | 5.9 | 3.9 | 11.7 |
| 0.10 | 1:1 | 13.0 | 6.7 | 4.7 | 13.4 |
| 0.15 | 1:0.5 | 14.2 | 6.8 | 5.0 | 12.1 |
| 0.15 | 1:1 | 15.4 | 7.8 | 6.1 | 19.0 |
| 0.15 | 1:2 | 8.5 | 4.4 | 2.1 | 4.8 |

³ The terms holemic and scalemic are now used to describe, respectively, a compound in optically pure form or in mixtures different from the racemic one. In the present case optical purity of products depends only on the optical purity of reagents and were not determined.

Table 6
Effect of substitution of Co(II) by Mn(II) on conversions

| % M of Mn ^{II} | % Conversion | | |
|-------------------------|--------------|----------------------|---------------------|
| | limonene (1) | α -pinene (2) | β -pinene (3) |
| 0 | 65 | 80 | 68 |
| 10 | 67 | 79 | 66 |
| 20 | 64 | 79 | 65 |
| 30 | 63 | 78 | 65 |

work are at least comparable with the selectivities of other systems described in the literature [32,49], which shows how difficult a task is the selective oxidation of β -pinene (3).

3.2. Effect of substituting Co(II) by Mn(II) on selectivities

To study the effect of adding Mn(II) (maintaining $[M^{II}]/[NaBr] = 1$), 10, 20, and 30% M of the Co(II) were substituted by Mn(II). As seen in Table 6, substitution of Co(II) by Mn(II) had no effect on conversions for limonene (1), α -pinene (2), and β -pinene (3)⁴. However, the use of the system Co(II)/Co(III)/Mn(II)/Mn(III) increased selectivity, probably by decreasing the oxidation potential of the catalytic system. Substitution of Co(II) by Mn(II) shifted selectivity towards alcohols and acetates (Figs. 1–3).

Thus, as shown in Fig. 1, autoxidation of limonene (1) led selectively to *trans*-carveol (7a), decreasing selectivity towards carveone (4) and 4-acetoxy-*p*-mentha-1,8-diene (12). It is worth pointing out that under these conditions, compounds produced from epoxides 14a and/or 14b i.e. compounds 10, 11 and 12 were not observed. Therefore, the selectivity of the system Co(II)/Co(III)/Mn(II)/Mn(III) was much greater towards the allylic oxidation of the endocyclic double bond than both epoxide forma-

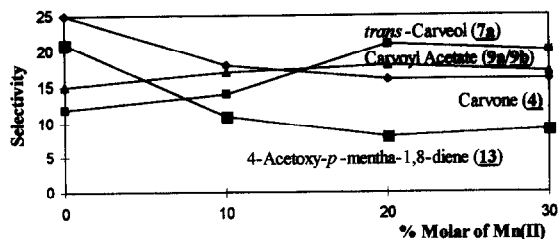


Fig. 1. Autoxidation of limonene. Effect of substitution of Co(II) by Mn(II).

tion and allylic oxidation of the exocyclic double bond in the case of limonene (1).

The autoxidation of α -pinene (2), under these conditions, also showed this pattern i.e. oxidation was selective towards alcohols and acetates. Therefore, a selectivity of 45–50% was obtained for *trans*-verbenyl acetate (17a), by substitution of 10 to 30% M of Co(II) by Mn(II), while keeping an almost constant (and low) selectivity towards myrtenal (6) and decreasing selectivity towards verbenone (5), as shown in Fig. 2.

The effect of substitution of Co(II) by Mn(II) on β -pinene (3) is worth pointing out. The Mn(II) increased selectivity towards *trans*-pinocarveol (16), from 8 to 16–18%, while decreased selectivity towards myrtenal (6) and α -terpinyl acetate (27), as shown in Fig. 3.

The overall effect of substituting Co(II) by Mn(II) was a selectivity tuning towards alcohols and acetates. Therefore, the results disclosed in the present work under the studied conditions,

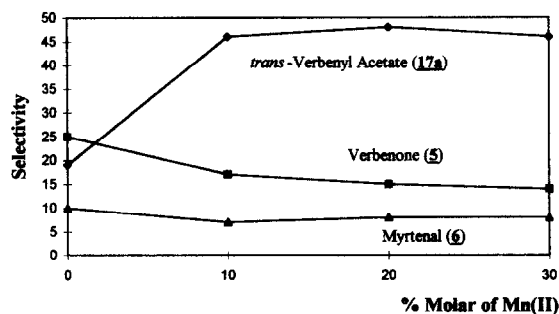


Fig. 2. Autoxidation of alpha-pinene. Effect of substitution of Co(II) by Mn(II).

⁴ Since the catalyst concentration used was very high, the reactions may be oxygen diffusion limited, so not increasing feedstock conversion.

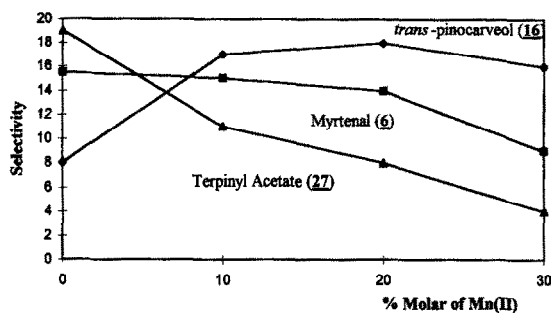


Fig. 3. Autoxidation of beta-pinene. Effect of substitution of Co(II) by Mn(II).

Co(II)/Mn(II)/Br, constituted an alternative and selective pathway towards alcohols and acetates derived from limonene (1), α -pinene (2) and β -pinene (3).

4. Conclusions

The overall effect of NaBr addition up to a $[\text{Co}(\text{OAc})_2]:[\text{NaBr}]$ ratio of 1:4 was to increase conversions, but decrease selectivity, thus confirming the effect of bromide ions on promoting these kind of reactions [15–17].

The present work confirmed the effect of bromide addition on conversions and selectivities for autoxidations catalysed by $\text{Co}(\text{OAc})_2$, in the presence of dioxygen. An optimal concentration of 0.15 M for $\text{Co}(\text{OAc})_2$ with a $[\text{Co}(\text{OAc})_2]/[\text{NaBr}] = 1$ was found yielding good selectivity to allylic oxygenated products.

Substitution of Co(II) by Mn(II) had no effect on conversions but shifted selectivity significantly towards alcohols and acetates. This favored *trans*-carveol (7a) and *trans*- and *cis*-carvoyl acetate (9a and 9b) from limonene (1); verbenyl acetate (17a) from α -pinene (2) and *trans*-pinocarveol (16) from β -pinene (3). Therefore, a selectivity tuning effect was made possible by varying $[\text{Mn}(\text{II})]$.

The effect of substituting Co(II) by Mn(II) would be related to a decrease in the overall oxidation potential of the system, disfavoring further oxidations and side reactions of the primary reaction products.

The results given in this work constitute new and reliable processes for the oxidation of monoterpenes leading to very important compounds for the flavor and fragrance industry.

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