Transition-Metal Catalyzed Autoxidation of *cis*- and *trans*-Pinane to a Mixture of Diastereoisomeric Pinanols

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Autoxidations of the pinanes, obtained after hydrogenation of naturally occurring *Pinus elliottii* oil, were performed with or without solvent, using the catalytic system $Co(OAc)_2/Mn(OAc)_2/NH_4Br$ in a 9:1:5 molar ratio, and dioxygen as the oxidant. The best selectivity for the pinanols was 71% (*cis*:*trans* ratio, 3:1) with 17% conversion. Autoxidations were also carried out in the absence of catalyst. The hydroperoxides formed with 17% conversion were decomposed with Na_2SO_3 and PPh_3, resulting in 62% pinanols (*cis*:*trans* ratio, 5:1). The pyrolysis of the pinanols at 600 °C and a contact time of 1.15×10^{-2} s/mol yielded 54% of linalool. The side products were mainly due to an "ene" reaction, giving diastereoisomeric 1,2-dimethyl-3-isopropenylcyclopentanols.

Keywords: *Catalytic oxidation; pinane; pinanol; pyrolysis; linalool*

INTRODUCTION

The acyclic linalool is an important alcohol being used as a feedstock for the manufacture of vitamin E and flowery-fresh-based fragrances. It is also used in flea shampoos and insecticidal sprays for house plants (Tsao and Coats, 1995). Currently, several large-scale processes have been developed for the synthesis of linalool starting with 2-methyl-2-hepten-6-one. Linalool can be easily obtained after ketone ethynylation with acetylene, followed by a selective hydrogenation (Pasedach et al., 1967). The synthesis from essential oils is also possible, and pinenes are among the preferred starting materials. Linalool can be obtained from pinene extracts by hydrogenation, followed by oxidation to the respective hydroperoxides which are reduced in a stoichiometric process (Fisher et al., 1953; Schmidt and Fisher, 1954). The alcohols formed are then pyrolyzed to linalool. The liquid-phase autoxidation of *cis*- (**1a**) and *trans*-pinane (**1b**) has already been studied, and the main products are pinane-2-hydroperoxides (**2**), derived from the oxidation of the tertiary carbon in position 2 (Brose et al., 1992) (Figure 1). When the autoxidation is carried out in the presence of catalytic amounts of azobisisobutyronitrile (AIBN), followed by a stoichiometric reduction with Na_2SO_3, *cis*- (**3a**) and *trans*-pinanol (**3b**) are obtained with a selectivity of up to 95%, using only **1a** as the substrate (Filliatre and Lalande, 1968). On the other hand, in the absence of AIBN, **3a** and **3b** are obtained with a selectivity of up to 85%, using Na_2SO_3 as the reducing agent and **1a** as the substrate (Brose et al., 1992). When the decomposition is carried out in the presence of sodium methylate to remove acids as they are formed, 50% of **3a** and **3b** are obtained among the products (Schmidt and Fisher, 1959).

The reports describing the autoxidation of pinanes are always related to the use of only **1a** or **1b** as the substrate. Therefore, no studies have been reported on the oxidation of mixtures of pinanes. We wish to report here our results on the catalytic oxidation of hydrogenated *Pinus elliottii* oil, which contains **1a** and **1b** as main components, with molecular oxygen. This procedure replaces the oxidation and reduction steps by only one catalytic step, using $Co(OAc)_2/Mn(OAc)_2$ as catalyst, directly producing the alcohols **3a** and **3b**. The mixture of oxidation products is then conveniently pyrolyzed to linalool (**4**) (Ohloff and Klein, 1962).

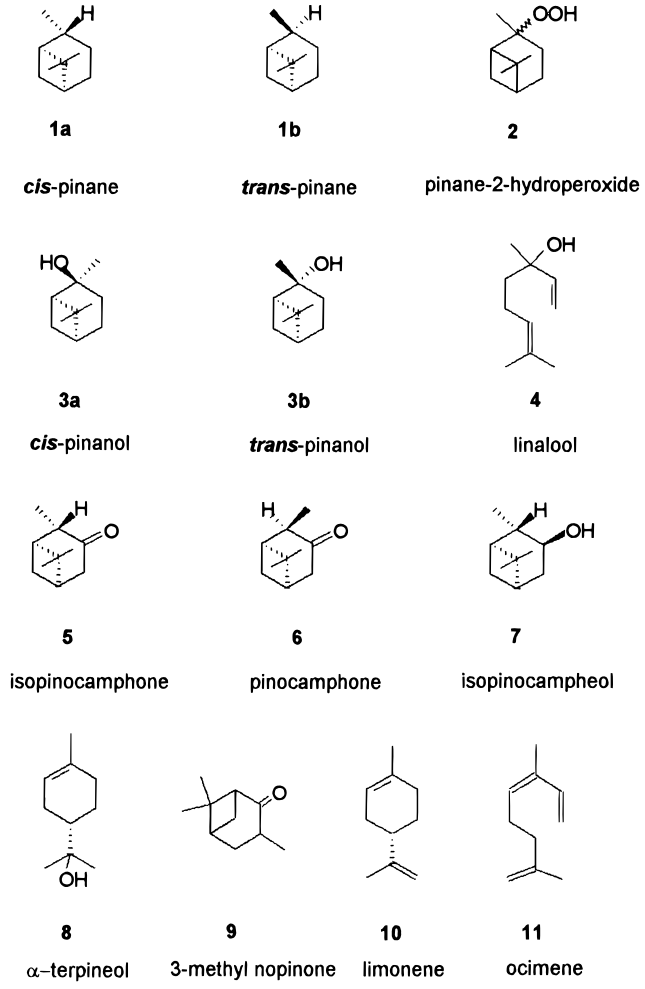

Figure 1. Formulas of the principal products.

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EXPERIMENTAL PROCEDURES

Materials. *P. elliottii* oil was obtained from Eucatex Química; α-pinene, linalool, and Pd/C were purchased from Aldrich Chemical Co. (Milwaukee, WI). Cobalt and manganese acetates were purchased from Alfa Products (Ward Hill, MA) and Fluka (Buchs, Switzerland). Chlorobenzene, dichloroethane, ammonium bromide, triphenylphosphine, sodium sulfite, and magnesium sulfate were purchased from Merck (Darmstadt, Germany).

Preparation of Pinanes. The pinanes were prepared by hydrogenation of 15 mL of *P. elliottii* oil (94% α- and β-pinene) in 10 mL of diethyl ether at room temperature in a 100 mL autoclave, using an H_2 pressure of 50 bar and 0.4 g of 5% Pd/C as catalyst. The conversion was quantitative, producing *cis*- and *trans*-pinane in a 4:1 ratio.

Preparation of Pinane Hydroperoxides. The oxidation reactions were performed in a 125 mL three-necked flask equipped with a reflux condenser, a thermometer, and a gas inlet tube with a glass frit. The flask was filled with 12.4 g of *cis*- and *trans*-pinane, magnetically stirred, and thermostated at 80 to 125 °C. Oxygen was then introduced into the system under different flow rates. The reaction was stopped at approximately 17% conversion, which was determined by iodometric titration during the course of the reaction. At higher conversions the selectivity for pinane hydroperoxides was significantly reduced.

Reduction of Pinane Oxidates with Sodium Sulfite. A 125 mL three-necked flask, equipped with a reflux condenser and a dropping funnel, was filled with 60 mL of a 1.27 mol L^{-1} aqueous solution of Na_2SO_3. The solution was heated to 60 °C, and 12 mL of pinane oxidates (previously weighed) was added under magnetic stirring over 4 h. The organic layer was separated, and the aqueous layer was extracted twice with 20 mL of diethyl ether. The organic extracts were combined and dried with $MgSO_4$, and the solvent was evaporated under reduced pressure.

Reduction of Pinane Oxidates with Triphenyl Phosphine. Into a 125 mL flask were introduced 50 mL of a solution of 0.09 M PPh_3 in dichloroethane and 3.7 g of the pinane oxidate. The mixture was magnetically stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure, and the product mixture was directly analyzed.

Catalytic Oxidation of Pinanes. In a 125 mL three-necked flask, equipped with a reflux condenser, thermometer and a gas inlet tube with a glass frit, 25 mL of chlorobenzene and 5.5 g of *cis*- and *trans*-pinane were added to 10 mol % of the catalyst [0.9 g of $Co(OAc)_2$/0.1 g of $Mn(OAc)_2$/0.2 g of NH_4-Br]. Some oxidations were carried out with 12.4 g of *cis*- and *trans*-pinane and 2 mol % of the catalyst. The reactions were performed under magnetic stirring and different oxygen flow rates (40−85 mL min^{-1}) for 16.5 h. The reaction mixture was filtered through neutral alumina, diluted with 25 mL of water, and then extracted three times with 20 mL of diethyl ether. The organic extracts were combined and dried with $MgSO_4$, and the solvent was evaporated under reduced pressure.

Pyrolysis of Pinanols. The unconverted pinanes were separated from the pinane oxidates by distillation under reduced pressure. The pinanol-containing oxidation mixture was pyrolyzed, using the apparatus described by Ohloff and Klein (1962), under an argon flow rate of 200 mL min^{-1} at approximately 1 mbar. Under these conditions the contact time of the pinane oxidates with the hot part of the reactor was 0.0115 s mol^{-1}.

Gas Chromatography (GC)/Mass Spectrometry (MS). The products were semiquantified by area normalization, using a Siemens SICHROMAT 1 gas chromatograph, equipped with a 30 m × 0.2 mm × 0.33 μm capillary column of crosslinked 5% phenylmethylsilicone (HP Ultra 2), coupled to a flame ionization detector. The temperature was programmed at 3 °C min^{-1} from 40 to 100 °C. The pinanes, pinanols, and linalool were identified by comparison of their retention times with those of authentic samples. The other products were identified using an HP 5890 gas chromatograph equipped with a 25 m × 0.2 mm × 0.33 μm capillary column of crosslinked methylsilicone (HP Ultra 1), coupled to a HP 5970B mass detector operating at 70 eV. The temperature was programmed at 3 °C min^{-1} from 40 to 100 °C. The mass espectra were compared with those of a Wiley NBS database showing similarity indices always higher than 90%.

Table 1. Noncatalytic Oxidations of *cis*- and *trans*-Pinane

temperature (°C)	80	80	100	125
reaction time (h)	16.5	16.5	3.5	3.5
conversion of pinanes (%)	14	17[a]	8	27
product distribution (%)[b]				
cis-pinanol (**3a**)	49	52	46	22
trans-pinanol (**3b**)	8	10	7	6
isopinocamphone (**5**)	2	1		
pinocamphone (**6**)	1	6	2	3
isopinocampheol (**7**)	4	4	5	4
α-terpineol (**8**)	4	4	5	
3-methylnopinone (**9**)	7	9	3	
others	27	26	27	44

[a] Conversion of pinanes after reduction with $P(C_6H_5)_3$. [b] Product distribution after reduction with Na_2SO_3 (12.4 g of pinanes, 85 mL min^{-1} O_2 flow).

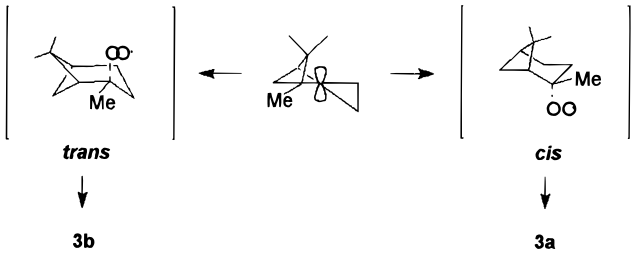

Figure 2. Intermediates for *cis*- and *trans*-pinanol.

Table 2. Product Distribution after Catalytic Oxidations of *cis*- and *trans*-Pinane in Chlorobenzene (5.5 g of Pinanes, 16.5 h, 80 °C)

oxygen flow (mL min^{-1})	40	85	85
substrate/catalyst molar ratio	10:1	10:1	50:1
conversion of pinanes (%)	17	27	21[a]
product distribution (%)			
cis-pinanol (**3a**)	54	32	5
trans-pinanol (**3b**)	17	17	11
isopinocamphone (**5**)	4	6	2
pinocamphone (**6**)	6	3	3
isopinocampheol (**7**)			
α-terpineol (**8**)			3
3-methylnopinone (**9**)		8	8
others	19	34	68

[a] Reaction carried out without solvent, using 12.4 g of pinanes.

RESULTS AND DISCUSSION

The *P. elliottii* oil, containing 94% α- and β-pinene, was hydrogenated at room temperature and 50 bar of hydrogen, giving a complete conversion of the pinenes to **1a** and **1b** (4:1 molar ratio). The oxidation reactions were first carried out in the absence of a catalyst and solvent, at temperatures in the range 80−125 °C. The hydroperoxides formed in these reactions were decomposed with Na_2SO_3 or PPh_3. The best selectivity for pinanols (Table 1) was found at 80 °C and 17% conversion, using PPh_3 as the reducing agent. Under these conditions, a 62% yield of **3a** and **3b** (5:1) was obtained, as well as some byproducts derived from the oxidation of secondary carbons. Conversions higher than 17% and reaction temperatures above 100 °C decrease the selectivity for pinanol. At 125 °C and 27% conversion, only 28% of pinanols were obtained as the desired products easily overoxidize to other products under these conditions. Brose et al. (1992) found similar results and

Table 3. Mass Spectral Data and Retention Times for the Volatiles Analyzed in the Catalytic Autoxidation of Pinanes

peak no.	retention time (min)	compound	*m*/*z* (relative abundance in %)
1	7.4	β-pinene	93 (100); 79 (30); 41 (30); 92 (25); 77 (19); 91 (15); 121 (12); 136 (10); 94 (5)
2	7.8	α-pinene	93 (100); 92 (42); 91 (41); 77 (31); 41 (28); 79 (27); 121 (11); 94 (8)
3	9.2	*trans*-pinane	55 (100); 41 (99); 95 (77); 67 (71); 82 (57); 81 (55); 83 (45); 69 (44); 138 (2)
4	9.7	*cis*-pinane	55 (100); 41 (97); 95 (77); 67 (71); 81 (57); 82 (54); 69 (46); 83 (42); 138 (2)
5	14.5	not identified	69 (100); 43 (89); 83 (89); 41 (68); 84 (58); 55 (40); 97 (37); 67 (19); 71 (17)
6	16.1	*trans*-pinanol	43 (100); 99 (57); 41 (53); 71 (46); 93 (42); 81 (37); 55 (36); 83 (23); 69 (20); 121 (18); 67 (17)
7	17.1	*cis*-pinanol	43 (100); 99 (66); 71 (48); 41 (45); 93 (40); 55 (33); 81 (30); 83 (24); 69 (20); 121 (17); 67 (14)
8	18.0	isopinocamphone	55 (100); 83 (90); 41 (80); 69 (66); 81 (22); 95 (18); 152 (8)
9	18.6	pinocamphone	55 (100); 41 (82); 69 (76); 83 (65); 95 (62); 43 (32); 67 (23); 81 (19); 152 (8)
10	19.4	not identified	43 (100); 85 (93); 41 (79); 55 (53); 95 (47); 67 (38); 79 (37); 83 (33)
11	20.2	not identified	83 (100); 55 (77); 41 (59); 95 (57); 57 (39); 109 (28); 43 (26); 137 (9); 152 (9)
12	20.5	verbenone	107 (100); 91 (71); 135 (66); 41 (57); 80 (50); 79 (49); 150 (43); 43 (33); 67 (28)

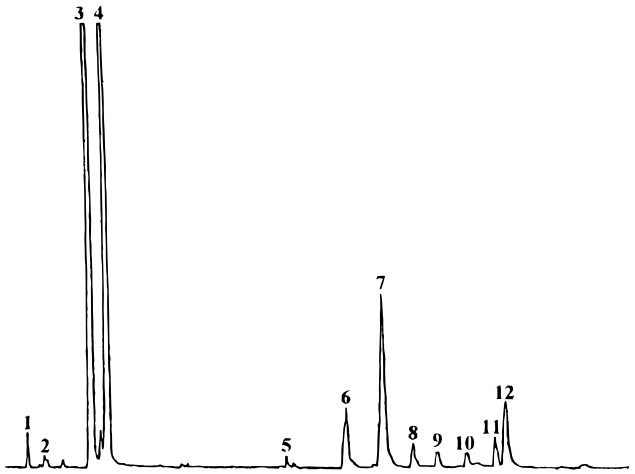

Figure 3. Gas chromatogram of the catalytic oxidation of pinanes.

reported that the fragmentation of the 2-pinanyl radical becomes more important than its combination with molecular oxygen in this temperature range. On the other hand, under a low oxygen flow (15 mL min^{-1}) no oxidation products were found. Limonene (**10**) was the main product, showing that the availability of oxygen is important for the formation of **3a** and **3b**.

Compound **3a** rather than **3b** is the favored oxidation product, *i.e.*, the attack of molecular oxygen at the 2-pinanyl radical occurs *trans* to the *gem*-dimethyl group. This preference is expected, since the *gem*-dimethyl group hinders the approach of the oxygen molecule from the same side. Furthermore, we suggest that the intermediate leading to **3a** is lower in energy than that leading to **3b**. The higher energy of the latter is related to its boat conformation, while the intermediate leading to **3a** prefers the chair conformation (Figure 2).

Catalytic oxidation produced a higher percentage of pinanols (Table 2), in addition to some byproducts derived from the oxidation of secondary carbons. The best results were obtained for a substrate/catalyst molar ratio of 10:1 using chlorobenzene as solvent. At 80 °C and 17% conversion, a selectivity for **3a** and **3b** (3:1) of 71% was obtained. The volatiles identified from the catalytic oxidation reaction are listed in Table 3 (a typical chromatogram is shown in Figure 3). The higher percentage of **3b**, formed in the catalytic process, may be explained by an easier attack of the molecular oxygen at the same side as the *gem*-dimethyl group, due to the interaction of the transition metal with the 2-pinanyl radical. Chlorobenzene was used as the solvent, not only to solubilize the catalyst but also to increase the oxygen content of the reaction mixture (Sawyer, 1991). The best results were obtained with an oxygen flow of 40 mL min^{-1}, which assures a sufficient oxygen supply. On the other hand, if under the same conditions the oxygen flow is reduced to 15 mL min^{-1}, we found ocimene (**11**) as the main product (60% selectivity) formed by substrate rearrangement.

The reaction mixture, containing approximately 70% **3a** and **3b**, was pyrolyzed in a quartz reactor at 600 °C, with a contact time of 0.0115 s mol^{-1}. Linalool (**4**) was obtained with 54% selectivity at conversions of up to 60%. Coxon et al. (1972) reported a selectivity for **4** of only 44%, but observed the same byproducts as obtained by us. The byproducts are mainly due to an "ene" reaction of **4**, giving diastereoisomeric 1,2-dimethyl-3-isopropenylcyclopentanols. Reduction of the contact time should further increase the selectivity of the pyrolysis reaction.

The catalytic oxidation of hydrogenated naturally occurring *P. elliottii* oil produces a mixture of diastereoisomeric pinanols in good yields, which can be easily converted to linalool. The overall selectivity for linalool from *P. elliottii* oil is 38% and does not involve the use of expensive reagents. As the catalytic oxidation eliminates the reduction step of the hydroperoxide and does not require reagents in stoichiometric amounts, it suggests an interesting alternative for the industrial production of linalool.

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