

# Palladium(II) catalyzed oxidation of naturally occurring terpenes with dioxygen

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## Abstract

Limonene can be efficiently and selectively oxidized by dioxygen at 60–80°C in glacial acetic acid containing LiCl, in the presence of the PdCl<sub>2</sub>–CuCl<sub>2</sub> catalytic combination, giving rise to the formation of *trans*-carveyl acetate as the major product. Several concurrent transformations of limonene occur in the reaction solutions, i.e., isomerization, acetic acid addition, and allylic oxidation. The effect of the reaction variables on the product distribution and reaction rate has been studied. The most favorable conditions for the carveyl acetate synthesis have been found. The reactions of  $\alpha$ -pinene and  $\beta$ -pinene under the same conditions yield a mixture of carveyl acetate,  $\alpha$ -terpenyl acetate, bornyl chloride, and fenchyl chloride. The activity of the Pd(OAc)<sub>2</sub>–LiNO<sub>3</sub> combination in the oxidation of limonene,  $\alpha$ -pinene, and  $\beta$ -pinene has also been examined.

**Keywords:** Olefin oxidation; Palladium catalysts; Monoterpenes; Dioxygen

## 1. Introduction

Oxidative functionalization of the sufficiently abundant monoterpenes represents a valuable route to extend the utilization of these cheap natural products. Some of their oxygenated derivatives are commercially important materials in pharmaceutical, perfume, and flavor preparations [1]. Allylic acetates are useful synthetic intermediates, in particular, due to the possibility of the selective and facile metal catalyzed substitution of the acetoxy group by other nucleophiles [2,3].

Although the reactions of olefin oxidation catalyzed by palladium(II) complexes have been

developed into important synthetic methods, there is very little information in the literature concerning their application to natural product synthesis. It was reported [4,5] that the acetoxylation of limonene in the PdCl<sub>2</sub>–CuCl<sub>2</sub>–(LiCl)–NaOAc/HOAc system using copper(II) chloride as a stoichiometric oxidant yields essentially *trans*-carveyl acetate and requires 48–72 h to reach a good yield.

The aim of the present study was to investigate the applications of the homogeneous catalytic combinations 'Pd(II) + reversible co-oxidant' for the oxidation of limonene (1),  $\beta$ -pinene (2), and  $\alpha$ -pinene (3) with dioxygen in acetic acid solutions. As reversible co-oxidants were used copper(II) chloride and lithium nitrate. We have found that limonene can be efficiently and

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selectively oxidized by dioxygen at 60–80°C in glacial acetic acid containing LiCl, in the presence of the PdCl<sub>2</sub>–CuCl<sub>2</sub> catalytic combination, resulting in *trans*-carveyl acetate as a major product. It has been observed that under the reaction conditions limonene undergoes various transformations, i.e., isomerization, acetic acid addition, and allylic oxidation. Efforts have been made to study the effects of the reaction variables on both the product distribution and the reaction rate and to find the most favorable conditions for the allylic oxidation.

## 2. Experimental

All reagents were purchased from commercial sources and used as received, unless otherwise indicated. *R*-(+)-limonene,  $\alpha$ -pinene, and  $\beta$ -pinene were distilled before use. CuCl<sub>2</sub>·2H<sub>2</sub>O was dehydrated by heating. LiCl was dried by heating. Glacial acetic acid was used as a solvent.

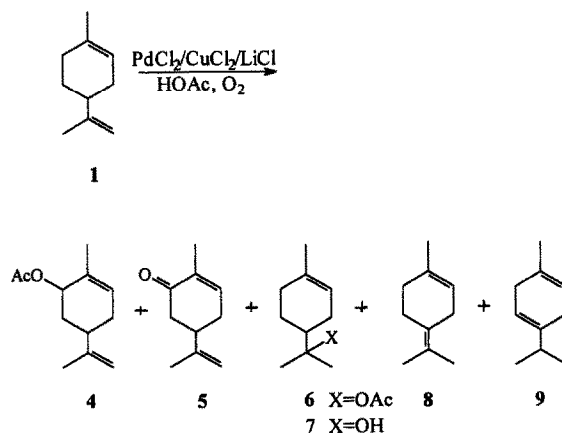
The reactions were carried out in a stirred glass reactor equipped with a sampling system and connected to a gas burette to monitor the oxygen uptake. The solution of the Pd(II) salt and either LiNO<sub>3</sub> or CuCl<sub>2</sub>–LiCl was stirred at the reaction temperature and an oxygen pressure of 0.1 MPa for 15 min. The olefin was added with a syringe using a sampling system, and the mixture was stirred for the reported time. The progress of the reaction was monitored both by capillary gas chromatography (GC) and by oxygen uptake. The products were analyzed by GC using a Shimadzu 14B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. After separation either by column chromatography or by extraction with a pentane–ether (1:1) mixture, the products were identified by NMR and GC-mass-spectroscopy on a Hewlett-Packard MSD 5890/Series II instrument. The structures of *trans*-carveyl acetate, *cis*-carveyl acetate, and  $\alpha$ -terpenyl acetate were also confirmed by chemical methods, i.e., saponification reactions resulting in *trans*-

carveol, *cis*-carveol and  $\alpha$ -terpineol, respectively. <sup>1</sup>H NMR spectra were in agreement with those reported in the literature [5–7]. NMR spectra were obtained using a Bruker CXP-400 spectrometer with tetramethylsilane as an internal standard and CDCl<sub>3</sub> as a solvent.

## 3. Results and discussion

We found that the solutions of limonene in glacial acetic acid containing PdCl<sub>2</sub>–CuCl<sub>2</sub>–LiCl rapidly consume dioxygen at 60–80°C and an oxygen pressure of 0.1 MPa. Several concurrent transformations of limonene occur in the reaction solutions: allylic oxidation resulting in carveyl acetate (**4**) and carvone (**5**); acetic acid and water (which presents as a trace contaminant) addition to the exocyclic double bond resulting in  $\alpha$ -terpenyl acetate (**6**) and  $\alpha$ -terpineol (**7**); and isomerization yielding mainly  $\alpha$ -terpinolene (**8**) and  $\gamma$ -terpinene (**9**) (Scheme 1).

The balance between the reaction pathways is delicate. The product distribution depends strongly on the reaction conditions and on the reaction time. The relative amounts of the products of the allylic oxidation (products **4** and **5**), addition (products **6** and **7**), and isomerization (products **8** and **9**) reactions vary from 70 to 95, 5 to 20, and 1 to 20%, respectively, at ca. 90%



Scheme 1.

conversion of limonene (Table 1). The formation of **4** is highly stereospecific (ca. 85% *trans*). The molar ratio of **4** with regard to **5** after the most of the runs is near 10, but in some cases is as high as 20. The ratio between the addition products **6** and **7** is influenced by the amounts of water in the reaction solutions. The glacial acetic acid was used as a solvent and the components of the catalyst were dried in order to minimize the formation of **7**. In the absence of PdCl<sub>2</sub>, no allylic oxidation products are detected, only the addition of acetic acid and water as well as limonene isomerization are observed. As can be seen (Table 1, run 1), the relative amounts of the isomerization and addition products are changed with reaction time. Judging from the data obtained, the existence of

the equilibrium between limonene and its isomers as well as between limonene and the addition products can be suggested.

The product selectivities change markedly in the course of the reaction. Fig. 1 demonstrates the variation of the product distribution as a function of time during the oxidation of limonene catalyzed by PdCl<sub>2</sub> (0.01 equiv.)–CuCl<sub>2</sub> (0.05 equiv.) in acetic acid solutions containing LiCl (0.8 equiv.). The products **4**–**9** are detected by GC, with the relative amounts of the allylic oxidation, addition, and isomerization products being 41, 30, and 29%, respectively, at 35% conversion of limonene. At the beginning of our work we thought that the selectivity for the allylic oxidation was fairly low. However, with increase in limonene con-

Table 1  
Oxidation of limonene with dioxygen catalyzed by PdCl<sub>2</sub>–CuCl<sub>2</sub> in acetic acid solutions <sup>a</sup>

Run	[PdCl <sub>2</sub> ] × 10 <sup>2</sup> (mol l <sup>-1</sup> )	[CuCl <sub>2</sub> ] × 10 (mol l <sup>-1</sup> )	[LiCl] (mol l <sup>-1</sup> )	Time (h)	Conversion (%)	Product distribution <sup>b</sup> (%)						Rate <sup>c</sup> × 10 <sup>3</sup> (mol l <sup>-1</sup> min <sup>-1</sup> )
						<b>4</b> <sup>d</sup>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	
1	0	2	0.5	1	32			44	13	29	14	0
				2	40			66	11	16	9	
				4	47			72	9	13	6	
				5	47			77	9	9	5	
				6	47			77	9	9	5	
2	1	2	0.5	3	96	87	4	4	2	2	1	6.8
3	1	1.5	0.6	4	93	83	5	5	3	3	1	5.5
4	1	1	0.7	4.5	96	80	6	6	2	3	2	4.1
5	1	0.75	0.75	5.5	90	72	8	7	3	8	2	3.2
6	1	0.5	0.8	1	50	38	11	19	4	22	8	1.7
				6	90	61	11	8	4	9	7	
7	2	0.5	0.17	1	52	77	13	7	1	1	tr <sup>h</sup>	4.1
				3.5	90	83	12	4	tr <sup>h</sup>	tr <sup>h</sup>	tr <sup>h</sup>	
8	1	0.5	0.19	0.5	29	73	12	7	3	5	tr <sup>h</sup>	3.4
				1.5	50	80	10	5	2	3	tr <sup>h</sup>	
				4	90	87	9	2	1	1	tr <sup>h</sup>	
9	0.5	0.5	0.2	2	55	73	9	13	2	2	1	2.4
10	0.25	0.5	0.2	3.5	55	71	7	13	4	3	2	1.5
11 <sup>e</sup>	1	0.5	0.19	1	30	74	9	7	1	7		2.3
12 <sup>f</sup>	1	0.5	0.19	1	24	73	10	9		8		1.5
13 <sup>g</sup>	1	0.5	0.19	1.5	20	72	8	10		10		1.0

<sup>a</sup> Reaction conditions: [limonene] = 1.00 mol l<sup>-1</sup>, 80°C, O<sub>2</sub> (0.1 MPa).

<sup>b</sup> Determined by gas chromatography.

<sup>c</sup> The rate of oxygen consumption at 15–30% conversion of limonene.

<sup>d</sup> 75–85% *trans* isomer.

<sup>e</sup> 70°C.

<sup>f</sup> 60°C.

<sup>g</sup> 50°C.

<sup>h</sup> Trace amounts.

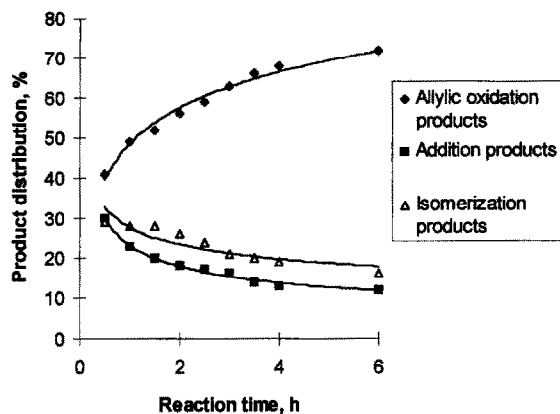


Fig. 1. Product distribution versus reaction time at limonene oxidation catalyzed by  $\text{PdCl}_2\text{-CuCl}_2$  in acetic acid. Reaction conditions are the same as in Table 1, run 6. Allylic oxidation products: 4 and 5; addition products: 6 and 7; isomerization products: 8 and 9.

version the rates of the addition and isomerization reactions decrease rapidly. The addition products are mainly formed at the beginning of the reaction (approximately for 1 h) and then their concentrations remain virtually unchanged. The initial increase and subsequent decrease in the concentrations of the isomerization products with the reaction time are observed. As a result, the selectivity for the allylic oxidation is significantly higher at longer reaction times. In the run presented in Fig. 1, e.g., the total selectivity for 4 and 5 increases from 41% at 35% conversion to 72% at 90% conversion of limonene.

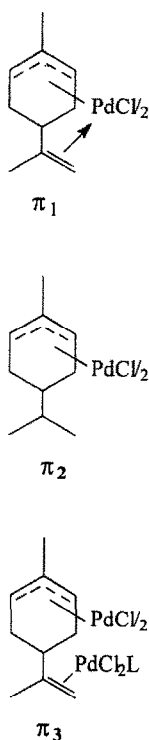
Our study revealed that the relative yields of the reaction products can be regulated by variation of the concentrations of the catalyst components. For example, a 61% selectivity for 4 is obtained after 6 h at limonene oxidation in acetic acid containing  $\text{PdCl}_2$  (0.01 equiv.),  $\text{CuCl}_2$  (0.05 equiv.), and  $\text{LiCl}$  (0.8 equiv.) at 90% conversion of limonene (Table 1, run 6). The addition and isomerization products are also formed (12% and 16%, respectively). The selectivity for the allylic oxidation products can be significantly improved by lowering the concentration of the chloride ions. With 0.19 equiv. of  $\text{LiCl}$  under the same conditions the time required for 90% limonene conversion de-

creases to 4 h and the selectivity for 4 rises up to 87%. The amounts of the addition and isomerization products are reduced to 3 and 1%, respectively (Table 1, run 8). The further decrease in the  $\text{LiCl}$  concentration is limited by the solubility of  $\text{PdCl}_2$  and  $\text{CuCl}_2$  in acetic acid. It should be mentioned that no chloride derivatives of limonene were detected among the reaction products.

To find the most favorable conditions for the allylic oxidation we investigated the effect of the reaction variables on the product distribution and reaction rate (Table 1). There is a first-order dependence of the allylic oxidation rate in the  $\text{Cu}$  concentration. The allylic oxidation rate is also proportional to the initial concentration of limonene in the range of 0.24 to 0.46  $\text{mol l}^{-1}$ . However, at higher concentrations the order with respect to limonene is decreased and is nearly zero in the range of 0.7 to 1.0  $\text{mol l}^{-1}$ . The initial limonene concentration of ca. 1.0  $\text{mol l}^{-1}$  is used in the most of the runs and the reaction rate is nearly constant until ca. 40% of limonene has been consumed. The effect of the reaction variables on the reaction rate was studied at low limonene conversions (15–25%). The rate of the allylic oxidation depends on the  $\text{Pd}$  concentration in the order of ca. 0.5, which is discussed below. The results obtained for the concentration ranges reported in Table 1 can be represented by the following rate expression: allylic oxidation rate  $\propto [\text{limonene}]^{1.0}[\text{Pd}]^{0.5}[\text{Cu}]^{1.0}$ . The range of the limonene concentration is mentioned above. The activation energy is equal to 37.2  $\text{kJ mol}^{-1}$  at the temperature between 50 and 80°C. It is worth noting that the rate of the formation of the addition products (6 and 7) hardly depends on both the  $\text{Cu}$  and  $\text{Pd}$  concentrations at all, and a kinetic study shows the orders of nearly zero.

The exocyclic double bond of limonene seems to play a key role in the allylic oxidation of the internal double bond. A  $\pi$ -allyl  $\text{Pd}$  complex  $\pi_1$  was suggested to be a reaction intermediate, with the coordination of the exocyclic double bond on the same  $\text{Pd}$  atom being of a critical

importance for the reactivity of this intermediate [5]. It was reported [5] that carvomenthene, synthesized from limonene by selective hydrogenation of the exocyclic double bond, did not undergo the allylic acetoxylation even at high temperature. The corresponding  $\pi$ -allyl Pd complex  $\pi_2$  was much more stable under the acetoxylation conditions compared to the analogous  $\pi$ -allyl complex  $\pi_1$  formed from limonene. As mentioned above, we have found that the reaction rate depends on the Pd concentration in the order of ca. 0.5. It may be explained by the formation of less active Pd  $\pi$ -allyl complexes, such as  $\pi_3$ , containing the second Pd atom bound to the exocyclic double bond, with an increase in the Pd concentration.



In the absence of  $\text{PdCl}_2$ , the fast limonene isomerization takes place in the reaction solutions yielding the isomers containing two internal double bonds: mainly, **8** and **9**. Anomaly high concentrations of **8** and **9** are seen at the beginning of the Pd-catalyzed reaction (up to

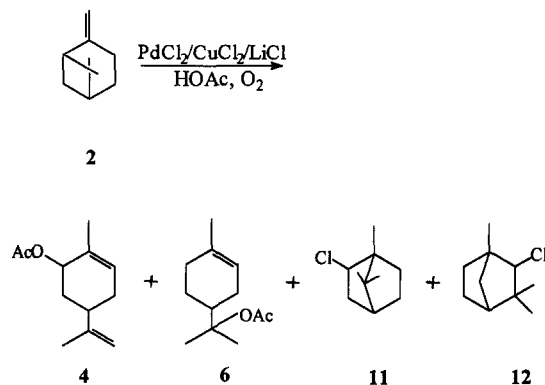
30% based on reacted limonene). However, no products of their oxidation are detected after the reaction, most likely, due to the low activity of the corresponding  $\pi$ -allyl Pd complexes, which contain no terminal double bond. The isomerization equilibrium at longer reaction times is shifted towards the formation of limonene and the concentrations of **8** and **9** decrease. Under the optimal conditions the final amounts of **8** and **9** do not exceed 1–3% based on reacted limonene.

The selectivity for the allylic oxidation products is also strongly influenced by relative concentrations of Pd, Cu, and chloride ions. The comparison was made at equivalent limonene conversions because the selectivities vary with the reaction time. Lowering the Pd concentration, at constant concentrations of Cu and chloride ions, exerts no effect on the addition reactions but decreases the rate of the allylic oxidation. This leads to the increase in the relative yields of the addition and isomerization products (runs 7–10, the data at ca. 50% limonene conversion). Both the isomerization and addition processes are relatively suppressed by increasing the Cu concentration, with the selectivity for **4** being significantly improved (runs 2–6, the data at ca. 90% limonene conversion). The product distribution virtually does not depend on both the initial limonene concentration in the range of 0.24 to 1.00 mol  $\text{l}^{-1}$  and the reaction temperature in the range of 50 to 80°C.

Table 2 shows the product distributions and substrate conversions at different reaction times during the reactions of  $\alpha$ -pinene and  $\beta$ -pinene in acetic acid solutions containing  $\text{PdCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{LiCl}$  at an oxygen pressure of 0.1 MPa. To facilitate a comparison between the various monoterpenes some data about the limonene oxidation under the same conditions are also included. A virtually complete conversion of all monoterpenes was observed after 3 h of reaction at 80°C. Limonene yields the allylic oxidation products **4** and **5** with 95% selectivity (run 1). In the presence of a large excess of chloride ions, the main products formed from

$\alpha$ -pinene and  $\beta$ -pinene, are **4** (ca. 85% *trans*), **6**, bornyl chloride (**11**), and fenchyl chloride (**12**) (runs 5 and 8, Scheme 2). Besides, the products of the skeletal rearrangement of pinenes, i.e., **1**, **8**, **9**, and camphene (**10**) are detected.

Very similar product distributions are obtained regardless of whether the starting material is  $\alpha$ -pinene or  $\beta$ -pinene. For example, the following reaction products are found after 3 h in acetic acid containing PdCl<sub>2</sub> (0.01 equiv.), CuCl<sub>2</sub> (0.1 equiv.), and LiCl (0.7 equiv.) at 80°C ( $\alpha$ -pinene/ $\beta$ -pinene): **4** (26/25%); **6** (21/19%); **11** (29/28%); **12** (10/15%); **7** (6/3%); **1** (4/3%); **10** (2/5%); and **9** (2/2%). GC analysis of the reaction mixture shows that at short reaction times the rates of the isomerization resulting mainly in limonene and HCl/HOAc addition reactions resulting in **6**, **11**, and **12** exceed significantly the rate of the formation of **4**. The latter seems to be a product of the allylic oxidation of the intermediary formed limonene. In the absence of PdCl<sub>2</sub>, no



Scheme 2.

allylic oxidation products are produced (runs 3 and 6). The selectivity for **4** increases with the increase in the concentrations of CuCl<sub>2</sub> and LiCl.

We have also examined the activity of the Pd(OAc)<sub>2</sub>-LiNO<sub>3</sub> combination in the oxidation of **1**, **2**, and **3**. This system catalyzes perfectly the oxidation of various olefins with dioxygen [8]. The results obtained are presented in Table

Table 2  
Reactions of monoterpenes in acetic acid solutions containing PdCl<sub>2</sub>, CuCl<sub>2</sub> and LiCl

Run	Olefin	Time (h)	Conversion (%)	Product distribution <sup>a</sup> (%)										
				1	2	4 <sup>b</sup>	5	6	7	8	9	10	11	12
1 <sup>c</sup>	limonene	3	80			85	10	5	tr. <sup>f</sup>	tr. <sup>f</sup>	tr. <sup>f</sup>			
2 <sup>d</sup>	limonene	3	95			75	6	7	3	6	3			
3 <sup>d,e</sup>	$\alpha$ -pinene	0.4	80	19				29	tr. <sup>f</sup>	10	3	7	24	8
		3	99	18		4		21	4	7	2	7	27	10
4 <sup>c</sup>	$\alpha$ -pinene	0.4	47	14				30	6	4	2	10	26	8
		3	99	14		6		30	5	3	2	7	26	7
5 <sup>d</sup>	$\alpha$ -pinene	0.4	83	16		6		27	4	8	5	0	25	9
		3	99	4		26		21	6	tr. <sup>f</sup>	2	2	29	10
6 <sup>d,e</sup>	$\beta$ -pinene	0.4	99	17	6			25	tr. <sup>f</sup>	8	4	5	13	22
		3	99	19		tr. <sup>f</sup>		23	tr. <sup>f</sup>	10	tr. <sup>f</sup>	6	27	15
7 <sup>c</sup>	$\beta$ -pinene	0.4	80	12	17			31	tr. <sup>f</sup>	6	2	4	18	10
		3	99	16	16	tr. <sup>f</sup>		34	tr. <sup>f</sup>	3	tr. <sup>f</sup>	tr. <sup>f</sup>	20	9
8 <sup>d</sup>	$\beta$ -pinene	0.4	99	16	10	tr. <sup>f</sup>		23		8	2	5	23	13
		3	99	3		25		19	3	tr. <sup>f</sup>	2	5	28	15

<sup>a</sup> Determined by gas chromatography.

<sup>b</sup> 75–85% *trans* isomer.

<sup>c</sup> Reaction conditions: [olefin] = 1.00 mol l<sup>-1</sup>, [PdCl<sub>2</sub>] = 10<sup>-2</sup> mol l<sup>-1</sup>, [CuCl<sub>2</sub>] = 5 × 10<sup>-2</sup> mol l<sup>-1</sup>, [LiCl] = 0.2 mol l<sup>-1</sup>, O<sub>2</sub> (0.1 MPa), 80°C.

<sup>d</sup> Reaction conditions: [olefin] = 1.00 mol l<sup>-1</sup>, [PdCl<sub>2</sub>] = 10<sup>-2</sup> mol l<sup>-1</sup>, [CuCl<sub>2</sub>] = 0.1 mol l<sup>-1</sup>, [LiCl] = 0.7 mol l<sup>-1</sup>, O<sub>2</sub> (0.1 MPa), 80°C.

<sup>e</sup> [PdCl<sub>2</sub>] = 0.

<sup>f</sup> Trace amounts.

Table 3

Reactions of monoterpenes in acetic acid solutions containing Pd(OAc)<sub>2</sub> and LiNO<sub>3</sub><sup>a</sup>

Run	Olefin	Conversion (%)	Product distribution <sup>b</sup> (%)
1	limonene <sup>c</sup>	4	<b>4</b> (60)+ <b>6</b> (40)
2	$\beta$ -pinene <sup>c</sup>	87	<b>6</b> (56)+ <b>1</b> (21)+ <b>3</b> (7)+ <b>10</b> (6) + <b>8</b> (6)+ <b>9</b> (3)+ <b>4</b> (traces)
3	$\alpha$ -pinene <sup>c</sup>	62	<b>6</b> (66)+ <b>1</b> (20)+ <b>10</b> (9)+ <b>8</b> (5)

<sup>a</sup> Reaction conditions: [olefin] = 1.00 mol l<sup>-1</sup>, [Pd(OAc)<sub>2</sub>] = 10<sup>-2</sup> mol l<sup>-1</sup>, [LiNO<sub>3</sub>] = 0.4 mol l<sup>-1</sup>, O<sub>2</sub> (0.1 MPa), 60°C, 2 h.<sup>b</sup> Determined by gas chromatography after the runs.<sup>c</sup> A very slow consumption of oxygen is observed in all the runs (lower than 0.4 × 10<sup>-3</sup> mol l<sup>-1</sup> min<sup>-1</sup>).

3. A very low limonene conversion is observed for 2 h at 60°C and oxygen pressure of 0.1 MPa in acetic acid containing Pd(OAc)<sub>2</sub> (0.01 equiv.) and LiNO<sub>3</sub> (0.4 equiv.). The small amounts of **4** (60%) and **6** (40%) are detected in the reaction mixture after the run (Table 3, run 1). Raising the reaction time to 4 h leads to no increase in the limonene conversion and causes the formation of a dark precipitate. The reaction with  $\alpha$ -pinene yields a mixture of **6** (66%), **1** (20%), **10** (9%), and **8** (5%); and that with  $\beta$ -pinene a mixture of **6** (56%), **1** (21%), **3** (7%), **10** (6%), **8** (6%), **9** (3%), and trace amounts of **4**. All the products observed except **4** are due to the acid catalyzed transformations of olefins: skeletal rearrangement and acetic acid addition. A very slow oxygen consumption is observed in all the runs (lower than 0.4 × 10<sup>-3</sup> mol l<sup>-1</sup> min<sup>-1</sup>).

Although nitrate ions readily oxidize the reduced Pd species in acetic acid solutions and are reoxidized back by dioxygen, neither the oxygen consumption nor the formation of the oxidation products in significant amounts are observed for all examined monoterpenes in the presence of the Pd(OAc)<sub>2</sub>-LiNO<sub>3</sub> combination. Heumann and co-workers reported in [9] that no oxidation of limonene with dioxygen occurs at the reaction in benzene, in the presence of PdCl(NO<sub>2</sub>)(CH<sub>3</sub>CN)<sub>2</sub>, whereas some other olefins, such as 4-vinyl-cyclohexene and nor-

bornene, give methylketones or epoxides in reasonable yields. As mentioned above we found that the rate of the allylic oxidation of limonene catalyzed by PdCl<sub>2</sub>-CuCl<sub>2</sub> is first order in the Cu concentration. These observations indicate that CuCl<sub>2</sub> has a behavior far exceeding that of a simple reoxidation agent. We suppose that one of the specific functions of CuCl<sub>2</sub> is to assist at the decomposition of the  $\pi$ -allyl Pd intermediate due to the formation of the bridging Pd-Cu complexes analogous to those reported in our previous publication [10]. The studies on the reaction mechanism are in progress.

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