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Selective palladium-catalysed functionalization of limonene: synthetic and mechanistic aspects

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Abstract

The scope and limitation of palladium-catalysed functionalization of limonene have been investigated. Various catalytic combinations were examined in order to select the most efficient system for conversion of this substrate into allylic esters, ethers or alcohols in acetic acid, methanol and water, respectively. It appears that under mild conditions the chemoselectivity was always high as only oxidation products were formed. Moreover, by a judicious choice of ligands and/or reoxidant of palladium, the reaction can be directed mainly toward the formation of functionalized compounds having their allylic double bond in either exocyclic or endocyclic position. In both cases, the *trans* isomer is the major product. In order to explain these results, a mechanism is proposed involving an external nucleophile attack on a bis (π-allyl–π-olefin) palladium complex, which was isolated under acetoxylation reaction conditions.

Keywords: Palladium; Limonene; Acetoxylation; Methoxylation; Allylic oxidation

1. Introduction

The regio and stereoselective allylic oxidation of olefins catalysed by palladium complexes, is now a very efficient process for the synthesis of allylic alcohols, esters and ethers [1–5].

Although the oxidation of simple alkenes or conjugated dienes has been extensively studied [6–12], little work has been devoted to the corresponding reactions using natural terpenic olefins [13–18]. These latter reactions could be valuable for the preparation of oxygenated derivatives of terpenes which are commercially important materials in pharmaceutical, perfume and flavour industries. Catalytic reactions represents an efficient alternative to the stoichiometric process [19] for the preparation of these compounds of high added value.

We report here the results of our investigation of the factors which influence the selectivity of the allylic oxidation of limonene catalysed by palladium. The mechanistic aspects of the reaction are also discussed through the characterization of organometallic complexes isolated during the reaction course, as well as via an

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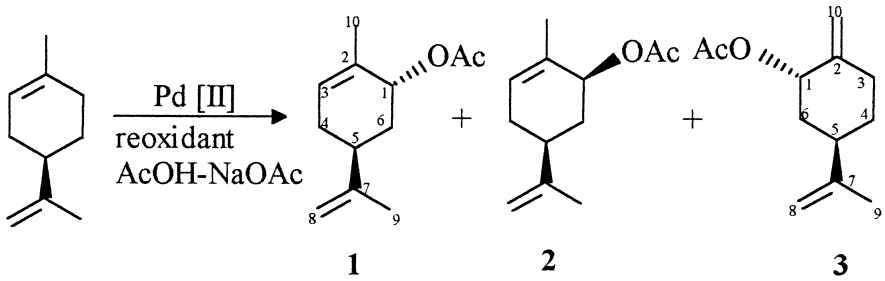


Scheme 1.

analysis of the observed regio-, stereo- and enantioselectivities.

2. Results and discussion

2.1. Allylic acetoxylation of limonene

We have previously reported [20] that (*R*)-(+)-limonene reacts in the presence of Pd(II) (catalytic) and a reoxidizing agent of palladium (stoichiometric) in acetic acid medium to give the allylic acetates **1**, **2** and **3** (Scheme 1). Under mild conditions (room temperature), the activity is moderate (48 to 72 h are needed to obtain a conversion of 50 to 95%) but the selectivity into oxidation products is very high as only low traces of isomerization or addition products are detected at the end of the reaction. However, at higher temperature, the formation of these side products notably increases. On the other hand, the distribution between the oxidation products is strongly dependent on the catalytic system. The classical Wacker catalyst ($PdCl_2$–$CuCl_2$–NaOAc) affords *trans*-carvyl acetate **1** as the major product (77%) and esters **2** and **3** (about 10–11% each) (Table 1, entry 1).

Replacing $CuCl_2$ and NaOAc by $Cu(OAc)_2$ and LiCl, respectively, (using different Cl-concentrations) improves the selectivity into the allylic ester **1** from 77 to 94% (Table 1, entries 1 and 2) at the expense of **2** which disappears almost totally. In the absence of chloride ions ($Pd(OAc)_2$–benzoquinone as reoxidant, stoichiometric vs. substrate), the activity notably decreases (compare Table 1, entries 2 and 3) and a complete change of selectivity occurs as the regioisomers **1** and **3** are produced in almost

Table 1
Allylic acetoxylation of limonene

No.	Catalytic system	Reaction time (h)	Conversion (%)	Product distribution[a] (%)		
				1	**2**	**3**
1	$PdCl_2$–$CuCl_2$–NaOAc[a]	48	90	77	12	11
2	$PdCl_2$–$Cu(OAc)_2$–LiCl[c]	48	92	94	0.8	5.2
3	$Pd(OAc)_2$–benzoquinone[d]	72	80	52	0	48
4	$Pd(OAc)_2$–LiCl–benzoquinone[e]	72	49	45	3	0

Conditions: solvent = AcOH; temperature = 20°C; limonene = 1 eq.
[a] Determined by GC.
[b] $PdCl_2$: 0.03 eq., $CuCl_2$: 1.8 eq., NaOAc: 2.6 eq.
[c] $PdCl_2$: 0.03 eq., $Cu(OAc)_2$: 2.7 eq., LiCl: 0.09 eq.
[d] $Pd(OAc)_2$: 0.05 eq., benzoquinone: 2 eq.
[e] $Pd(OAc)_2$: 0.05 eq., benzoquinone: 2 eq., LiCl: 2 eq.

Table 2
Limonene acetoxylation in chloride-free acetic acid, product distribution vs. time

Time (h)	Conversion (%)	Product distribution[a] (%)		
		1	**2**	**3**
10	13	46	0	54
24	38	50	0	50
48	63	43	0	57
72	80	52	0	48

Conditions: $Pd(OAc)_2$ = 0.05 eq.; benzoquinone = 2 eq.; limonene = 1 eq.; solvent = AcOH; temperature = 20°C.
[a]Determined by GC.

identical amount all over the reaction time (see Table 2). The addition of chloride ions (LiCl) to this last system leads to a further decrease in the activity and has the effect to restore a high selectivity into acetate **1** (Table 1, entry 4 and Fig. 1). Moreover, the GLC analysis of the reaction medium shows the presence of two supplementary products identified as the *trans* **4** and *cis* **5** carvyl chlorides (see Scheme 2).

As these chloride derivatives could be the intermediates of the reaction, their formation during the reaction course was examined. Table 3 shows that **4** and **5** quickly appear with a high selectivity in *trans* form (the ratio **4** vs. **5** is always higher than 8). Their concentrations reach a maximum and then decrease slowly to the benefit of the esters **1** and **2**.

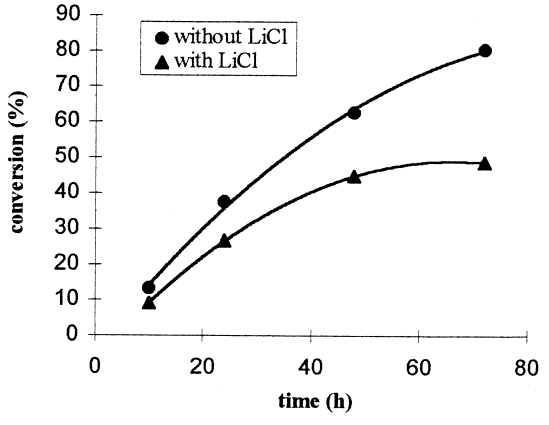
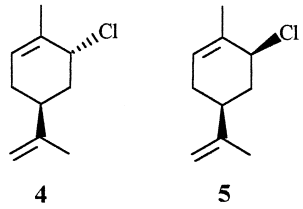


Fig. 1. Acetoxylation of limonene catalysed by the $Pd(OAc)_2$–benzoquinone system. Effect of chloride ions.



4 **5**

Scheme 2.

2.2. Chloride–acetate exchange reaction

In order to account for the above results, the reactivity of the chloride **4** under the acetoxylation conditions was studied and the results are summarized in Table 4.

In the absence of palladium at room temperature, the conversion is very low and only 10% of the initial chloride substrate reacted after 72 h to yield the esters **1** and **2** in a 1/1 ratio. At a higher temperature, (60°C) the conversion reaches 50% after 4 days and the isomer **2** becomes the main product (ratio **2**/**1** = 76/24).

Upon $Pd(OAc)_2$ addition, a higher conversion is observed. However, the activity is still moderate and lower or of the same order of magnitude as the one observed during the direct acetoxylation of limonene with the $Pd(OAc)_2$–benzoquinone–LiCl system. It is also noteworthy that pure *trans*-carvyl chloride (synthesized from α-pinene [21]) reacts to afford a mixture of *trans* and *cis* acetates **1** and **2** and not the

Table 3
Limonene acetoxylation in the presence of chloride ligands, product distribution vs. time

Time (h)	Conversion (%)	Product distribution[a] (%)				
		4	**5**	**1**	**2**	**3**
10	9	100	0	0	0	0
24	27	69	6	25	0	0
48	45	56	7	37	0	0
72	49	48	4	45	3	0
168	89	11	0	78	6	5

Conditions: $Pd(OAc)_2$ = 0.05 eq.; benzoquinone = 2 eq.; limonene = 1 eq.; solvent = AcOH; LiCl = 2 eq.; temperature = 20°C.
[a]Determined by GC.

Table 4
Treatment of *trans*-carvyl chloride **4** in acetic acid medium

Time (h)	Conversion (%)	Product distribution[a] (%)				
		4	**5**	**1**	**2**	**3**
7	13	87	0	11	2	0
24	26	74	0	21	5	0
48	38	62	0	29	9	0
72	40	60	0	29	11	0

Conditions: $Pd(OAc)_2$ = 0.05 eq.; benzoquinone = 2 eq.; *trans*-carvyl chloride **4** = 1 eq.; solvent = AcOH; temperature = 20°C.
[a]Determined by GC.

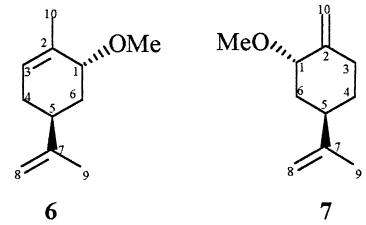
expected pure *trans*-ester **1**, with a selectivity in **1** lower than that observed during the acetoxylation of limonene under the same conditions (see Table 4). From these results, since (i) the reaction rate of exchange is very low in the absence of palladium and (ii) the selectivity is different from that observed during direct acetoxylation, we can conclude that this exchange is catalysed by palladium, but this process accounts only for a minor part in the overall acetoxylation reactions.

2.3. Allylic methoxylation and oxidation

In order to determine the scope and limitation of this methodology to functionalize limonene, attempts have been made to extend this reaction to other nucleophiles than OAc^-.

2.3.1. Methoxylation

We have previously described the methoxylation of limonene catalysed by palladium [20].



6 **7**

Scheme 3.

As can be seen in Table 5, Pd(II)–Cu(II) systems which catalyse acetoxylation of limonene, are ineffective toward its methoxylation. The same remark can be made about the Pd to benzoquinone system. However, in this case addition of *p*-toluenesulfonic acid (PTSA) leads to a great improvement of the activity, i.e., 85% conversion is obtained after 6 h with 0.1 equivalent of PTSA with respect to substrate (Table 5, entry 2).

In this reaction, the regioselectivity is reversed in comparison with the one observed in acetoxylation; the ether **7** with the exocyclic double bond is the major product with a selectivity higher than 90%. It should also be noted that **7** and its isomer **6** which are the sole reaction products, exhibit a *trans* configuration (see Scheme 3).

2.3.2. Oxidation

According to the fruitful results obtained in methoxylation, the behaviour of limonene in the presence of water was examined with the aim to obtain allylic alcohols of more potential interest

Table 5
Allylic methoxylation of limonene

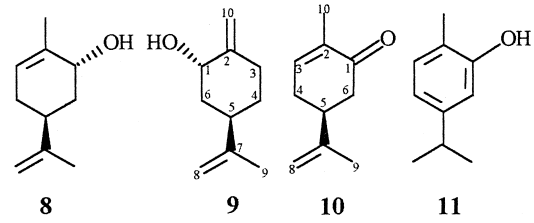
No.	Catalytic system	Reaction time (h)	Conversion (%)	Product distribution[a] (%)	
				6	**7**
1	$Pd(OAc)_2$–benzoquinone	48	0	–	–
2	$Pd(OAc)_2$–benzoquinone–PTSA	6	85	7	93
3	$Pd(acac)_2$–benzoquinone–PTSA	12	80	7	93
4	Li_2PdCl_4–benzoquinone–PTSA[b]	24	90	87	tr[c]

Conditions: solvent = AcOH; temperature = 20°C; limonene = 1 eq.; Pd(II) = 0.05 eq.; benzoquinone = 2 eq.; PTSA = 0.1 eq.
[a]Determined by GC.
[b]*cis* Isomer of **6** in 3%, others: dimethoxy in 10% (acid catalysis).
[c]Trace amounts.

than ethers. It appears that at room temperature, the reactivity is always very low. At higher temperature (80°C), the presence of a cosolvent such as acetone or dioxane is required to solubilise the olefin in the aqueous phase. Without cosolvent as well as in pure cosolvent, virtually no reaction takes place (see Table 6, entries 1 and 2). The nature of cosolvent, as long as it allows to dissolve the olefin in the aqueous phase, has little influence on the conversion (Table 6, entries 3 and 5) and the best results are obtained for a cosolvent vs. water ratio of about 1/1. Higher or lower contents bring about lower conversions (compare Table 6, entries 3 and 4).

On other hand, the selectivity depends mainly on the nature of the catalytic system and particularly on that of palladium salt and reoxidant. Thus, when the reaction is performed in a mixture of water and acetone, with the same catalytic system as the one used in methoxylation reactions (i.e., $Pd(OAc)_2$–benzoquinone–PTSA), a mixture of *trans*-carveol, **8** and its isomer **9** is obtained (Scheme 4) (90% conversion after 7 h, 42 and 35% selectivity into **8** and **9**, respectively). Replacing $Pd(OAc)_2$ by Li_2PdCl_4 gives carvone **10** as the major product (73% selectivity) together with carveol (5%) and carvacrol **11** (12%) (in this case, the alcohol **9** is not detected) (Table 7, entry 1).

Fig. 2 which depicts the variation of the products distribution as a function of time during the oxidation of limonene under the above conditions (with Li_2PdCl_4 as catalyst), shows that carveol formed at the early stage of the reaction, reaches a maximum after ca. 1.5 h and slowly disappears. In contrast, carvone and carvacrol are formed more slowly but their amount increases regularly. This observation seems to indicate that carveol behaves as an intermediate for the production of carvone and carvacrol. To verify this assertion, pure carveol was allowed to stir under the same conditions as those used in oxidation of limonene. In the absence of palladium or with $Pd(OAc)_2$, only very low conversions are observed whereas with Li_2PdCl_4, carveol is easily oxidized into carvone, next slowly converted into carvacrol (Fig. 3).



Scheme 4.

The concentration of PTSA has a lower influence on the oxidation activity than in methoxylation reactions. Indeed, the conversion varies in the range 78 to 90% for a PTSA vs. substrate ratio varying between 0 to 0.1 and remains constant beyond this value. Furthermore, the

Table 6
Effect of the solvent during limonene oxidation

No.	Solvent	Conversion (%)	Time (h)	Product distribution[a] (%)		
				8	**10**	**11**
1	acetone	0	48		no reaction	
2	water	9	48		not determined	
3	water/acetone (1/1)	90	7	5	73	12
4	water/acetone (1/4)	50	7	15	30	6
5	water/dioxane (1/1)[b]	99	12	tr[c]	71	13

Conditions: temperature = 80°C; limonene = 1 eq.; Li_2PdCl_4 = 0.03 eq.; benzoquinone = 2 eq.; PTSA = 0.1 eq.
[a] Determined by GC.
[b] Formation of 16% of α-terpineol.
[c] Trace amounts.

Table 7
Effect of the catalytic systems on the oxidation of limonene

No.	Catalytic system	Conversion (%)	Time (h)	Product distribution[a] (%)			
				8 (*trans*/*cis*)	**9** (*trans*)	**10**	**11**
1	Li_2PdCl_4–benzoquinone	90	7	5/0	tr[c]	73	12
2	Li_2PdCl_4–benzoquinone/MnO_2 (0.05/1)[b]	97	30	56/2	25	2	tr[c]
3	Li_2PdCl_4–$CuCl_2$	79	24	2/1	28	4	12
4	$Pd(OAc)_2$–benzoquinone	90	7	42/0	35	tr[c]	tr[c]
5	Li_2PdCl_4–MnO_2	20	24	low selectivity			
6	Li_2PdCl_4–H_2O_2			no reaction			
7	Li_2PdCl_4–$Cu(OAc)_2$			no reaction			

Conditions: solvent = water/acetone (1/1); temperature = 80°C; limonene = 1 eq.; Pd(II) = 0.03 eq.; LiCl = 0.09 eq.; reoxidant = 2 eq.; PTSA = 0.1 eq.
[a] Determined by GC.
[b] Isomerisation of limonene (11%).
[c] Trace amounts.

concentration of PTSA has a greater effect on the selectivity into carvacrol, the transformation of carvone into this compound being catalysed by H^+ ions [22]. However, even at high PTSA contents and long reaction times, the selectivity into carvacrol only reaches a maximum of 37% for 1 eq. of PTSA/substrate after 24 h.

These observations account for the difference in selectivity observed between Li_2PdCl_4 and $Pd(OAc)_2$ and allow to establish the relationship of the main reaction products as outlined in Scheme 5.

Finally, with other oxidants than benzoquinone: $Cu(OAc)_2$, H_2O_2 or MnO_2, almost no reaction took place. $CuCl_2$ is slightly more active but 24 h are needed to reach 80% conversion with the following product distribution: **8** = 2/1% (*trans*/*cis*); **9** = 28%; **10** = 4% and **11** = 12%; It is also noteworthy that a combination of Li_2PdCl_4 (catalytic)–benzoquinone (catalytic) and MnO_2 (stoichiometric) leads to 97% conversion after 30 h with selectivities of 56, 2 and 25% into *trans* **8**, *cis* **8** and **9**, respectively (Table 7, entry 2).

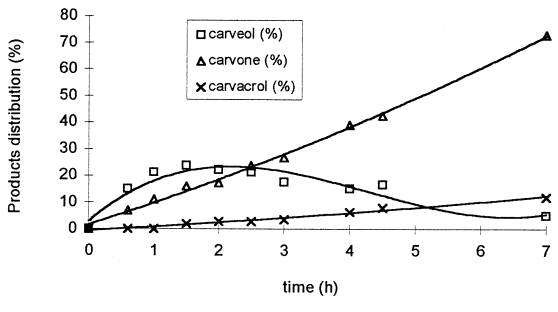


Fig. 2. Oxidation of limonene catalysed by the Li_2PdCl_4–benzoquinone system.

2.4. Mechanistic aspects

Although the allylic oxidations of olefins catalysed by Pd(II) have been intensively studied, its mechanism is not yet perfectly clear [6–8,23,24]. According to the products distribution, two major mechanisms have been proposed (see Scheme 6). One involves as initial step the formation of a π-allyl palladium as intermediate followed by a nucleophilic attack

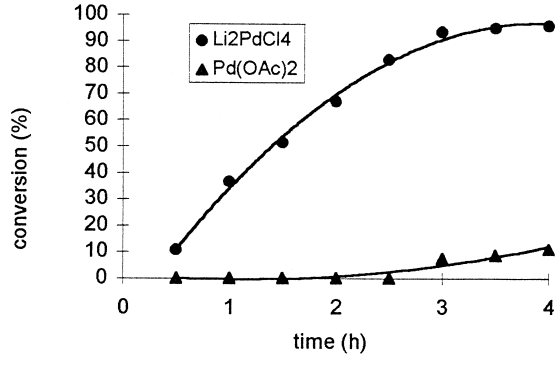
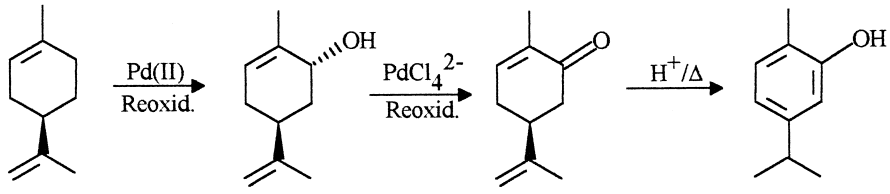
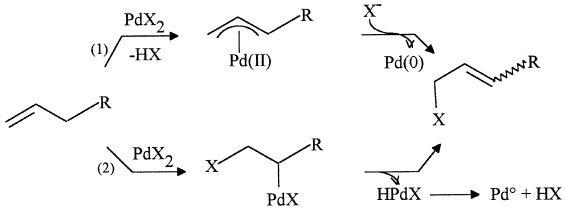


Fig. 3. Oxidation of carveol into carvone. Influence of the catalytic precursor.



Scheme 5.



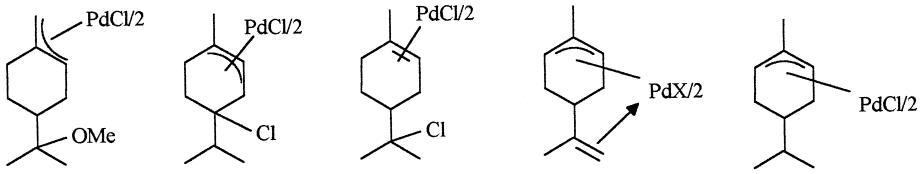
Scheme 6.

on the less substituted carbon (path 1). The other one proceeds via palladation of alkene followed by β-H elimination (path 2). The second way seems more probable in the case of linear terminal olefins [25] whereas with internal or cyclic alkenes, the two paths may compete [8].

Owing to its two double bonds having different reactivity, limonene is expected to lead to different intermediates according to the experimental conditions. Actually, in methanol and in the presence of Na_2PdCl_4, the formation of complexes **12** and **13** was reported whereas in chloroform, the π-olefin palladium complex **14** was isolated (Scheme 7) [26]. In the same way, various palladium complexes of 2 and 3-carenes were obtained [27,28]. Their characterisation shows that the regioselectivity of their synthesis depends on the reaction medium.

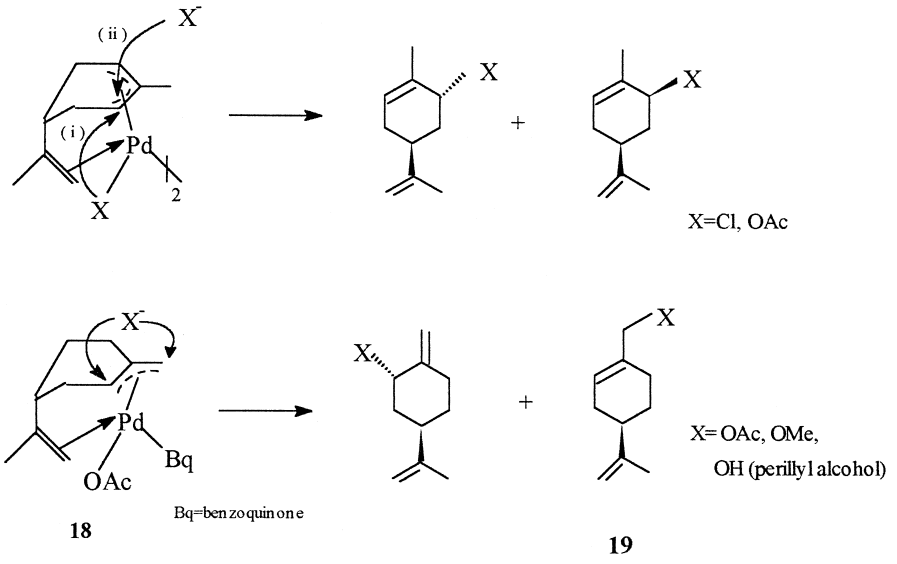
In our case, it should be noted that similar regio and stereoselectivities are obtained in acetoxylation, methoxylation or oxidation of limonene according to the presence or the absence of the chloride anions. Indeed, in the presence of Cl^-, functionalized products predominantly exhibit endocyclic allylic double bond whereas without Cl^-, the reaction products with exocyclic double bond are largely or mainly obtained. In both cases, *trans* isomers are preferentially formed. From these features, one can propose that the same intermediates are involved in these three processes.

Furthermore, we have previously reported [20] that in acetic medium and in the presence of NaOAc, palladium chloride (stoichiometric) reacts with limonene to give a palladium complex isolated by quenching the reaction after 2 h. The spectral data of this Pd species are in agreement with those of complex **15** (Scheme 7) in which palladium is linked to limonene through a π-allyl and a π-olefin bond. Complex **15** is highly reactive in solution. This observation is probably in connection with the coordination of



12 **13** **14** **15** X=Cl **16** X=OAc **17**

Scheme 7.



Scheme 8.

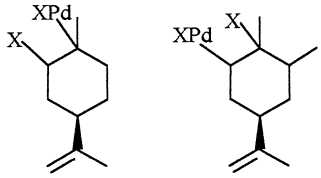
the exocyclic double bond of limonene with palladium. Indeed the analogous π-allyl Pd complex **17** (Scheme 7) synthesized from carvomenthene resulting from selective hydrogenation of the exocyclic double bond of limonene [29] is much more stable than **15** and carvomenthene does not give allylic acetoxylation under the same conditions as for limonene.

This complex **15** reacts with OAc^- in acetic acid to produce mainly the ester **1**, while in the absence of nucleophile, it quickly decays to produce *p*-cymene and Pd^o. Furthermore, this species is an efficient catalyst of acetoxylation of limonene in the presence of Cu^{2+} as oxidant.

From these observations we can reasonably assume that **15** is an intermediate in acetoxylation reactions conducted with the system Pd(II)–Cu(II)–NaOAc. From **15**, two nucleophilic attacks leading to the esters **1** and **2** must be considered: (i), *cis* migration of the nucleophile coordinated to palladium (giving the *cis* isomer); (ii), external attack (*trans* substitution) on the less hindered side of the intermediate [23,24]. The abundance of the *trans* isomer in the reaction products indicates that this second way is the major process when the acetoxylation reaction occurs in the presence of Cl^-. Without Cl^- (in reactions conducted with the system $Pd(OAc)_2$–benzoquinone), the regioselectivity totally changes, the ester **3** being formed in about equal amounts as **1**. Although various attempts to isolate an intermediate failed under these conditions, according to the large predominance of the isomer *trans* **1** vs. *cis* **2**, we think that the ester **1** is probably formed, as already stated, via a π-allyl Pd complex such as **16**. Moreover, this assumption is in accordance with a recent report of Grennberg et al. [9] who have unambiguously proved the formation of a (π-allyl)-palladium as intermediate in the quinone-based palladium-catalysed allylic acetoxylation of cyclohexene. On the other hand, nucleophilic attack on **16** cannot explain the formation of ester **3**. This compound could arise via the exocyclic π-allyl Pd, **18** (Schemes 8 and 9).

The fact that compounds **3**, **7** and **9** resulting from acetoxylation, methoxylation and oxidation conducted with enantiomeric pure limonene exhibit an optical activity [1] in contrast with

[1] An $[\alpha]_D^{20} = +37.8$ ($c = 1.56$, MeOH), -43 ($c = 1.13$, MeOH) and -72 ($c = 0.4$, MeOH) is observed for **3**, **7** and **9**, respectively, starting from *R*-(+)-limonene (**3**) or S-(−)-limonene (**7** and **9**).



20 **21**

Scheme 9.

both carvyl derivatives or carveol, proves that the latters derive from a symmetrical intermediate unlike the former. This is in agreement with the proposed mechanism.

The formation of σ-palladium species such as **20** and **21** could also be considered as plausible intermediates. Nevertheless, as complex **20** is not symmetrical, it should yield after β-H elimination optically active reaction products. The fact that neither carvyl acetate, carveol nor the ether **6** are optically active and that a selective β-H elimination giving only the products **3, 7** and **9** (with allylic exocyclic double bond) is unlikely, allows us to rule out this possibility. In addition, compound **19** (X = OAc) was detected as traces in many reactions, its formation cannot be explained from complex **20**.

In the same way, since no product of the menthol series was observed in these reactions, the involvement of intermediates previously reported such as **13**, can be ruled out.

Finally, it appears that the reaction rate of limonene functionalization with the system Pd(II)–benzoquinone increases with the benzoquinone amount whereas the decrease in benzoquinone concentration had a detrimental effect on the oxidation step of carveol into carvone. Thus, benzoquinone does not only play the role of a simple reoxidizing agent of Pd^{o} but probably behaves also as a ligand. Indeed, various complexes in which benzoquinone is coordinated to Ni, Pd and Pt have been described [30] and the same behaviour of benzoquinone was reported during catalytic diacetoxylation of dienes, via its coordination to the metal [23,24].

Acetation ions are weak ligands which easily dissociate and thus, the equilibrium (Eq. (1)) is shifted to the right for a low amount of benzoquinone.

$$(\text{Allyl})\text{PdX}_2 + \text{Bq} \rightleftharpoons (\text{Allyl})\text{Pd(Bq)X} + \text{X}^- \quad (1)$$

where Bq = benzoquinone, X = Cl or OAc

From the fact that chlorides ions are much more coordinated than acetate, they shift the equilibrium to the left and the reaction rate decreases. In contrast, an increase in benzoquinone shifts the equilibrium to the right and increases consequently the reaction rate. These explanations are in agreement with our observations (Table 1, Fig. 1).

3. Conclusion

Palladium-catalysed acetoxylation, methoxylation and oxidation of limonene are highly regio and stereoselective reactions. This selectivity is strongly dependant on the reaction conditions. Among the different plausible reaction ways, a process involving the formation of π-allyl–π-olefin palladium complexes as intermediate seems the most probable. The fact that the functionalization of chiral limonene occurs to give racemic regioisomers of carvyl skeleton or carvone whereas regioisomers with exocyclic double bond exhibit an optical activity, is in agreement with this hypothesis.

4. Experimental

(*R*)-(+)- or (*S*)-(−)-limonene were purchased from Janssen Chimica. Solvents were commercial grade. Catalysts and co-catalysts (benzoquinone, $CuCl_2$, $CU(OAc)_2$) were used without further purification. The reaction mixtures were analysed on a Varian 3400 Cx series chromatograph equipped with an FID detector, using silica capillary columns B.P. 20 (25 m × 0.25 mm, SGE) or CPSil5CB (10 m × 0.33 mm, Chrompack). The following conditions

were employed: temperature programmed from 70°C to 200°C/at 3°C/min, nitrogen carrier gas pressure = 5 psi; detector temperature 300°C; injector temperature 250°C.

Liquid chromatographies were performed on silica gel (Merck 60, 220–440 mesh; eluents: hexane–ether). ^{1}H, ^{13}C and 2D NMR were recorded on a Brucker AM 400 in solution by using TMS as an internal standard. A DB1 (30 m × 0.25 mm) capillary column was used for GC/MS coupled analyses with a Concept II spectrometer (Kratos Analytical).

4.1. General procedure for acetoxylation of (R)-(+)-limonene

Acetic acid (25 ml) was introduced in a two-necked round-bottomed flask fitted with a reflux condenser. Palladium catalyst and co-catalyst were introduced (see Table 1), and the mixture was then stirred for 30 min at 85°C. The reaction mixture was cooled to room temperature and the (*R*)-(+)-limonene was added. The resulting mixture was kept at the same temperature for the with Et_2O (2 ml), washed with water (0.5 ml), dried over $MgSO_4$ and analysed by GC. After completion, a 50:50 mixture of hexane/ether (30 ml) was added and the solution was stirred for 30 min. The organic phase was separated and collected and the remaining acetic acid phase was diluted with saturated NaCl (10 ml) and extracted with hexane/ether (3 × 30 ml). The combined extracts were neutralized with a saturated solution of $NaHCO_3$, dried over $MgSO_4$ and evaporated under reduced pressure. The reaction products were then isolated by column chromatography on silica using various ratios of EtOAc/hexane.

4.2. General procedure for limonene methoxylation

Pd(II) (0.18 mmol), *p*-benzoquinone (778 mg, 7.2 mmol) and *p*-toluene sulfonic acid (68.5 mg, 0.36 mmol) were dissolved in methanol (20 ml) and stirred at room temperature for 15 min. Limonene (500 mg, 3.6 mmol) was then added. Stirring was continued for the indicated period of time (Table 5) at this temperature. The reaction's progress was followed by GC. Once the reaction was complete, water (5 ml) and hexane/ether (9:1, 20 ml) were added. The phases were separated, and the aqueous one was extracted with hexane/ether (9:1, 3 × 20 ml). The combined organic phases were washed with water (5 ml) and 2 M NaOH (3 × 5 ml); the last alkaline washing was performed with the addition of small portions of $NaBH_4$ until the organic phase was colorless, and water (5 ml). After drying ($MgSO_4$), the solvent was removed under reduced pressure.

4.3. General procedure for limonene oxidation

A mixture of catalyst and co-catalyst (see Table 7) was dissolved into 20 ml of a water/acetone mixture (1:1), and added into a 100-ml round-bottomed flask fitted with a reflux condenser. After stirring at 80°C for 30 min, limonene was added, and the mixture was stirred for the reported time. After cooling to room temperature, the solution was passed through a short silica gel column using hexane/ether (1:1) as eluent. The organic phase was washed successively with 5 ml of water, 10 ml of 2 M NaOH and 5 ml of water and dried over $MgSO_4$. The solvent was removed under reduced pressure.

Pure products were isolated by column chromatography of the crude material on silica gel using various ratios of ether/hexane as the eluent, and were characterised by proton and carbon NMR spectroscopies and mass spectrometry. The structures of the products were established unambiguously by one dimensional NMR spectra which were in agreement with those reported in the literature [31]. The structures of *cis*-carvylacetate **2**, *cis*-carvylmethylate and *cis*-carveol were confirmed by chemical methods [20]. The *trans* stereochemistry of the products **1**, **3**, **6**, **7**, **8** and **9** was determined by the observation of four carbon resonances (1, 4,

Table 8
Selected $^{1}H/^{13}C$ NMR data of funtionalized products

Products	δH_1 (δC_1) (ppm)	δH_4 (δC_4) (ppm)	δH_5 (δC_5) (ppm)	δH_6 (δC_6) (pmm)	J (Hz)
1	5.26 (70.58)	4 ax:1.83 4 eq:2.21 (30.94)	2.32 (35.86)	6 ax:1.63 6 eq:1.95 (33.71)	$J_{1-6ax} = 4.2$; $J_{5-6ax} = 13$; $J_{5-4ax} = 11.2$; $J_{1-6eq} = 2.56$; $J_{5-6eq} = 4.2$; $J_{5-4eq} = 4.2$.
3	5.43 (74.3)	4 ax:1.34 4 eq:1.87 (32.4)	2.45 (31.0)	6 ax:1.58 6 eq:2.02 (37.0)	$J_{1-6ax} = J_{1-6eq} = 3.1$; $J_{5-6ax} = J_{5-4ax} = 12.09$ $J_{5-6eq} = J_{5-4eq} = 3.38$
6	3.46 (77.55)	4 ax:2.0 4 eq:1.8 (30.9)	2.3 (35.23)	6 ax:1.35 6 eq:2.04 (30.9)	$J_{1-6ax} = 3.3$; $J_{5-6ax} = 9.44$; $J_{5-4ax} = 11.98$ $J_{1-6eq} = 3$; $J_{5-6eq} = 2.6$; $J_{5-4eq} = 2.3$.
7	3.68 (81.3)	– 30.57	2.46 (39.02)	– 38.8	$J_{1-6eq} = 2.99$; $J_{5-6ax} = J_{5-4ax} = 12.4$
8	4.0 (68.53)	4 ax:1.5 4 eq:1.85	2.3 (35.2)	6 ax:1.6 6 eq:1.9 (36.7)	$J_{1-6ax} = J_{1-6eq} = 2.2$; $J_{5-6ax} = 13.4$ $J_{5-4ax} = 11$;
9	4.35 (72.4)	1.27 (32.57)	2.5 (38.1)	6 ax:1.5 6 eq:2.0 (39.0)	$J_{1-6ax} = 3.1$; $J_{5-6ax} = 12.2$; $J_{6eq-6ax} = 15.3$
10	– (199.6)	4 ax:2.32 4 eq:2.48 (43.02)	2.58 (42.35)	6 ax:2.22 6 eq:2.48 (31.12)	$J_{5-6ax} = J_{5-4ax} = 12.82$ $J_{5-6eq} = 1.8$, $J_{6ax-6eq} = 15.87$
11	– (153.61)	6.77 (118.83)	– (148.47)	6.68 (113.10)	

5 and 6) and measuring dipolar coupling between homonuclear $^{1}H-^{1}H$ spin pairs constants (J_{ax-ax}, J_{ax-eq}, J_{eq-eq}). Selected $^{1}H/^{13}C$ NMR Data of functionalized products are given in Table 8.

4.4. Synthesis of pure trans-carvyl chloride

Trans-carvyl chloride was prepared according to reference [20] by treatment of α-pinene (20 mmol) by dimethyl sulfoxide (80 mmol) and phosphorus oxychloride (20 mmol) in methylene chloride for 30 min over a temperature range of -20°C to 20°C. At the end of the reaction, a solution of $NaHCO_3$ was added, and the mixture was extracted by $CHCl_3$. The organic phase was dried and the solvent removed leading to virtually pure *trans*-carvyl chloride in quantitative yield.

4.5. Synthesis of π-allyl palladium complexes

Bis(π-allyl limonene) dichlorodipalladium **15**: To a red solution of Li_2PdCl_4 ($PdCl_2$: 129.5 mg, 0.73 mmol–LiCl: 63.5 mg, 1.5 mmol) and sodium acetate (540 mg, 6.58 mol) in acetic acid (20 ml) was added (*R*)-(+)-limonene (300 mg, 2.2 mmol). The reaction mixture was stirred at room temperature for 2 h and the pale yellow solution further extracted with hexane/Et_2O (1/1) (3×30 ml). The organic phase was washed with water, dried ($MgSO_4$) and the solvent evaporated under vacuum at room temperature to yield an orange oil. After addition of heptane (3 ml) and cooling (-5°C), 140 mg of yellow solid **15** was obtained. Due to its low stability, NMR of **15** was quickly performed in toluene d_8 under nitrogen at 243 K. ^{1}H NMR δ 4.28 (t, 2H, $J = 6.24$ Hz), 4.26 (s, 1H), 1.20 (s, 3H), 1.04 (s, 3H); ^{13}C NMR δ 147.51, 116.72, 111.21, 76.65, 39.26.

Bis(π-allyl menthene) dichlorodipalladium **17**: the same procedure as for the preparation of **15** was used, yielding 72% of a yellow solid. The NMR spectra were performed in $CDCl_3$ at room temperature.

^{1}H NMR δ 4.71 (s, 2H), 2.01 (s, 3H), 0.83 (d, $J = 6.63$ Hz, 6H); ^{13}C NMR δ 114.99,

78.62, 43.28, 53.29, 31.91, 22.73, 20.08. Anal. Found: C, 42.23; H, 6.17; Cl, 12.47; Pd, 38.00. $C_{20}H_{34}Pd_2Cl_2$ calcd.: C, 43.03; H, 6.14; Cl, 12.70; Pd, 38.12%).

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