

Palladium catalyzed oxidation of monoterpenes: novel oxidation of myrcene with dioxygen

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Abstract

Myrcene can be efficiently and selectively oxidized by dioxygen in glacial acetic acid containing LiCl, in the presence of the PdCl₂–CuCl₂ catalytic combination, yielding two isomers of a new functionalized monoterpene, i.e., 3-(1-acetoxy-1-methylethyl)-1-vinylcyclopentene and 4-(1-acetoxy-1-methylethyl)-1-vinylcyclopentene, as major products. These compounds have a pleasant scent with a flower or fruit tinge and could be used as components of synthetic perfumes. The activities of Pd(OAc)₂–LiNO₃, Pd(OAc)₂–Cu(NO₃)₂ and Pd(OAc)₂–benzoquinone systems in myrcene oxidation have also been examined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Myrcene; Dioxygen; Oxidation

1. Introduction

Functionalization of the sufficiently abundant monoterpenes represents a promising route to extend the potential use of these inexpensive natural products. Some of their oxygenated derivatives are commercially important materials in the pharmaceutical, perfume and flavor industries [1,2]. We have previously reported that allylic acetates, alcohols, aldehydes and esters can be obtained in good yields and in some cases with high stereoselectivity by the catalytic oxidation or carbonylation of some monoterpenes, such as limonene, β-pinene, and camphene [3–9]. Recently, we have also developed an efficient method for the hydration/acetoxylation of limonene, β-pinene and α-pinene into one of the top 30 com-

monly used flavor compounds, i.e., α-terpineol, and its acetate, using a heteropolyacid catalyst [10].

The reactions of olefin oxidation by palladium salts may be made into a catalytic process by use of reversible co-oxidants, with CuCl₂ being the most conventional one (Wacker-type catalyst). Although these processes represent a commercially valuable pathway to produce important oxygenated products from olefins and dioxygen, the most abundant and cheapest oxidant, their applications to natural product synthesis are rather scarce [3,4,9,11–14]. We previously reported the selective PdCl₂/CuCl₂ catalyzed oxidation of limonene, but failed to extend this method to the bicyclic monoterpenes, such as β-pinene and camphene, because of skeletal rearrangements promoted by CuCl₂ [3,4]. Next, we developed a CuCl₂-free system for the selective oxidation of β-pinene and camphene into allyl and glycol derivatives, respectively, using H₂O₂ as a final oxidant and Pd(OAc)₂ as catalyst [4]. In a further study, we investigated

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the applications of the Pd(II)/NO₃⁻ catalytic system, which in some cases offers valuable alternatives to the Wacker catalyst, for the oxidation of camphene by dioxygen and developed a selective process for the synthesis of new diterpene derivatives [9].

The aim of this study was to investigate the applications of the homogeneous catalytic combinations “Pd(II) + reversible co-oxidant” for the oxidation of myrcene (**1**) with dioxygen in acetic acid solutions. The reversible co-oxidants used were copper(II) chloride, lithium nitrate and copper(II) nitrate. Benzoquinone, which acts as a final oxidant, was also tested for palladium reoxidation. Myrcene (**1**), a naturally occurring acyclic polyunsaturated monoterpene, is easily available by industrial process of pyrolysis of β -pinene, one of the major constituents of pine turpentine [1]. Palladium-promoted reactions of myrcene have been little studied hitherto [15–22]. Various acyclic and cyclic (π -allyl)-palladium complexes formed from myrcene have been isolated and characterized, with their structure depending on the solvent used [16–18]. Oxidation of myrcene by palladium complexes resulting in citral and nerol has been described mainly in the patent literature [18–22]. Here we wish to report a novel palladium catalyzed oxidation of myrcene by dioxygen resulting in new functionalized monoterpenes with cyclopentane structure, which have a pleasant scent with a flower or fruit tinge and could be used as components of synthetic perfumes. Substituted cyclopentanes are basic frameworks for numerous natural monoterpenes including those important for the flavor and fragrance industry [23], e.g., campholenic aldehyde, which is used for the manufacture of sandalwood fragrances with an exotic woody scent.

2. Experimental

All reagents were purchased from commercial sources and used as received, unless otherwise indicated. Myrcene was distilled before use. CuCl₂·2H₂O was dehydrated by heating and LiCl dried by heating. Glacial acetic acid was used as a solvent. Benzoquinone was purified by column chromatography (silica).

The reactions were carried out in a glass reactor equipped with a magnetic stirrer and followed by

measuring the dioxygen uptake (if any) and/or by gas chromatography (GC) using a Shimadzu 14B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. Bornyl acetate was used as the internal standard. The solution of the catalytic system (Pd(II) salt and either LiNO₃, Cu(NO₃)₂, benzoquinone or CuCl₂-LiCl) in glacial acetic acid was stirred at the reaction temperature and an oxygen pressure of 0.1 MPa for 15 min. Then, myrcene was added and the mixture was stirred. Products were identified by GC/MS (Hewlett-Packard MSD 5890/Series II, 70 eV). New product **2** was isolated as a mixture **2a/2b** by column chromatography (silica) and identified by GC/MS, IR (Mattson FTIR 3000/Galaxy Series), ¹H- and ¹³C-NMR spectroscopy (Bruker DRX-400, tetramethylsilane, CDCl₃, COSY, HMQC and DEPT experiments). Spectral simulations performed with the ADC/CNMR program were in agreement with the spectra observed.

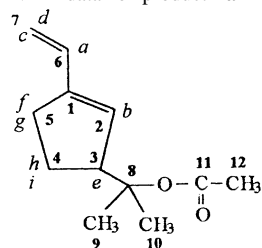
Spectroscopic data for **2** (light yellow oil): ν_{\max} (film), cm⁻¹: 3100 [ν (=C-H)], 3025 [ν (=C-H)], 1745 [ν (C=O)], 1650 [ν (C=C)], 1600 [ν (C=C)], 1255 [ν (C-O-C)], 1140 [ν (C-O-C)], 1025 [δ (=C-H)], 905 [δ (=C-H)]; (*m/z*/relative intensity) for **2a**, 3-(1-acetoxy-1-methylethyl)-1-vinylcyclopentene (shorter GC retention time): 134/70 [M - HOAc]⁺, 119/100 [M - HOAc-CH₃]⁺, 93/96, 92/18, 91/90, 79/23, 77/41, 65/16, 59/58 (OAc); **2b**, 4-(1-acetoxy-1-methylethyl)-1-vinylcyclopentene: 179/1 [M-CH₃]⁺, 134/32 [M - HOAc]⁺, 119/100 [M - HOAc-CH₃]⁺, 93/14, 92/20, 91/59, 79/13, 77/16, 65/16, 59/12 (OAc). For NMR data, see Tables 1 and 2.

Spectroscopic data for **3b**, 4-(1-chloro-1-methylethyl)-1-vinylcyclopentene (light yellow oil): (*m/z*/relative intensity): 172/2 [M + 2]⁺, 170/6 [M]⁺, 134/20 [M - HCl]⁺, 119/74 [M - HCl-CH₃]⁺, 93/25, 92/45, 91/100, 79/34, 77/41, 69/21, 65/20. δ_{H} (ppm): 1.59 (s, 3H, Me), 1.57 (s, 3H, Me), 2.47–2.53 (m, 4H, -CH₂-), 2.60–2.64 (m, 1H, -CRH-), 5.07 (d, 1H, -CH=CHH, *J* = 17.3 Hz), 5.08 (d, 1H, -CH=CHH, *J* = 10.0 Hz), 5.64–5.66 (m, 1H, -CH=), 6.50 (dd, 1H, -CH=, *J* = 10.0, 17.3 Hz).

3. Results and discussion

Myrcene (**1**) is a naturally occurring acyclic monoterpene containing three carbon-carbon double

Table 1
NMR data for product **2a**



Carbon atom	Hydrogen atom	$\delta(^1\text{H})$ (ppm) ^a	$\delta(^{13}\text{C})$ (ppm)	COSY-H/H ^b	NOE correlations ^c
1			144.63		
2	b	5.62 (d (br), $^3J_{b-c} = 1.9$)	130.82	e, c, d, f, g	With a and e; no NOE with c and d
3	e	3.33 (ddd, $^3J_{b-e} = 1.9$, $^3J_{e-i} = 6.1$, $^3J_{e-h} = 8.9$)	55.52	b, h, i	
4	h	2.01 (ddt, $^3J_{e-h} = 8.9$, $^2J_{h-i} = 9.3$, $^3J_{f-h} = 4.0$, $^3J_{g-h} = 4.0$)	24.83	e, f, g, i	
	i	1.74 (ddt, $^3J_{g-i} = 13.1$, $^3J_{f-i} = 6.1$, $^3J_{e-i} = 6.1$, $^2J_{h-i} = 9.3$)		e, f, g, h	
5	f	2.45–2.52 (m)	30.46	b, h, i	
	g	2.45–2.52 (m)		b, h, i	
6	a	6.57 (dd, $^3J_{a-c} = 16.9$, $^3J_{a-d} = 10.7$)	133.90	c, d	With b, c and d
7	<i>c</i> _{cis}	5.09 (d, $^3J_{a-c} = 16.9$)	114.53	a, b, d	With a, f and g; no NOE with b
	<i>d</i> _{trans}	5.08 (d, $^3J_{a-d} = 10.7$)		a, b, c	With a, f and g; no NOE with b
8			84.76		
9	H-9	1.40 (s)	23.38		
10	H-10	1.41 (s)	23.47		
11			170.55		
12	H-12	1.97 (s)	22.53		

^a Resonance multiplicities and coupling constants (Hz): (s) singlet, (d) doublet, (dd) doublet of doublets, (ddd) doublet of doublets of doublets, (ddt) doublet of doublets of triplets, (m) multiplet, (br) broadened.

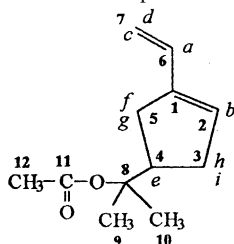
^b Weak correlations are italicized.

^c Selected NOE correlations are given.

bonds, two of them being conjugated. Occurrence of various concurrent transformations is expected in acetic acid solutions of palladium salts, thus making it difficult to achieve a high selectivity for one particular reaction. We found that solutions of myrcene in glacial acetic acid, containing PdCl₂–CuCl₂–LiCl, rapidly consume dioxygen at 30–80 °C and an oxygen pressure of 0.1 MPa. Two major products **2a** and **2b** with very small difference in GC retention times were detected and isolated as a mixture **2a/2b** (ca. 1.2/1 mol mol⁻¹) from the reaction solution by column chromatography. Their chemical nature has been elucidated firstly by GC–MS and IR and then by NMR spectroscopy. All three methods clearly show the presence of the acetate group in both products.

Mass spectra of **2a** and **2b** are very similar, indicating that these compounds seem to be closely related isomers. However, their fragmentations are quite different from those of the compounds with acyclic (“myrcene-like”) or cyclohexane (“limonene-like”) skeleton, which are the expected products of myrcene transformations [1]. In both spectra, peaks at *m/e* = 59, due to the formation of acetate ion, and at *m/e* = 134, corresponding to the loss of acetic acid molecule, are observed. This gives for the original molecules the molecular weights of 194 corresponding to the products of the addition of acetic acid to **1** with the abstraction of two hydrogen atoms, i.e., oxidative acetoxylation. IR spectrum of the mixture **2a/2b** is very characteristic for the esters and shows the strong C=O stretching absorption

Table 2
NMR data for product **2b**



Carbon atom	Hydrogen atom	$\delta(^1\text{H})$ (ppm) ^a	$\delta(^{13}\text{C})$ (ppm)	COSY-H/H ^b	NOE correlations ^c
1			142.03		
2	b	5.65–5.68 (m)	129.82	<i>c, d, f, g, h, i</i>	With a; no NOE with e, c and d
3	h	2.35–2.45 (m)	32.11	b, e	
	i	2.35–2.45 (m)		b, e	
4	e	2.78 (tt, $^3J = 7.9$, $^3J = 9.1$)	47.61	<i>f, g, h, i</i>	
5	f	2.35–2.45 (m)	34.16	b, e	
	g	2.35–2.45 (m)		b, e	
6	a	6.52 (dd, $^3J_{a-c} = 17.2$, $^3J_{a-d} = 11.0$)	133.96	c, d	With b, c and d
7	<i>c_{cis}</i>	5.06 (d, $^3J_{a-c} = 17.2$)	113.84	a, b, d	With a, f and g; no NOE with b
	<i>d_{trans}</i>	5.05 (d, $^3J_{a-d} = 11.0$)		a, b, c	With a, f and g; no NOE with b
8			83.82		
9	H-9	1.40 (s)	23.56		
10	H-10	1.41 (s)	23.65		
11			170.61		
12	H-12	1.98 (s)	22.48		

^a Resonance multiplicities and coupling constants (Hz): (s) singlet, (d) doublet, (dd) doublet of doublets, (tt) triplet of triplets, (m) multiplet.

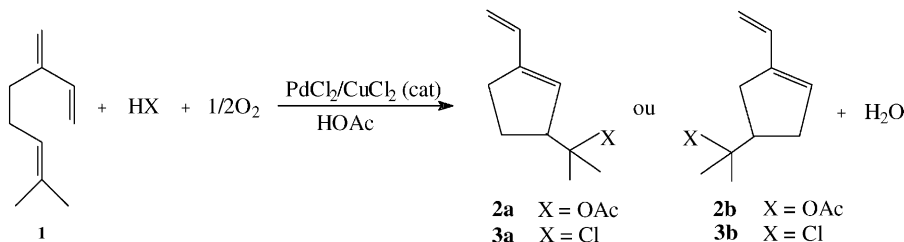
^b Weak correlations are italicized.

^c Selected NOE correlations are given.

at 1745 cm^{-1} and two strong bands for the C–O stretching vibration at 1255 (broad) and 1140 cm^{-1} [24–26]. In addition, this spectrum exhibits absorptions due to the C=C fragments at: 3100 cm^{-1} [$\nu(\text{C-H})$], 3025 cm^{-1} [$\nu(\text{C-H})$], 1650 cm^{-1} [$\nu(\text{C=C})$], 1600 cm^{-1} [$\nu(\text{C=C})$], 1025 cm^{-1} [$\delta(\text{C-H})$] and 905 cm^{-1} [$\delta(\text{C-H})$] [24–26]. In the $^1\text{H-NMR}$ spectrum of the mixture **2a/2b** two singlets at δ 1.97

and 1.98 ppm corresponding to the methyl protons of the acetate groups and no $-\text{CH-O}-$ signals are observed, indicating that these products are tertiary acetates. Based on an analysis of the GC–MS, IR, ^1H - and ^{13}C -NMR spectroscopy data we proposed the structures given in Scheme 1 for products **2a** and **2b**.

The assignment of the hydrogen and carbon resonances (Tables 1 and 2) was carried out by COSY



Scheme 1.

(^1H , ^1H), HMQC (^1H , ^{13}C) and DEPT NMR. Compounds **2a** and **2b** differ from each other in the position of the endocyclic double bond: in **2a** the isopropyl group is attached to C-3, whereas in **2b** to C-4. This structural difference was clearly revealed by COSY experiments. The strong cross peak observed in the COSY spectrum of **2a** confirms that vinylic proton b, which appears in the ^1H -NMR as a doublet, is coupled with methine proton e. Such a correlation is not detected for isomer **2b**. Instead, proton b in **2b** is coupled with methylene protons at C-3, h and i. The correlation between two methylene groups (pairs of protons f/g and h/i) is observed in **2a** but not in **2b**. These observations strongly support the positions of the double bond in the proposed cyclopentene structures. Allylic coupling between protons b and f/g results in significant broadening of the signals from b protons in both **2a** (doublet at 5.62 ppm) and **2b** (multiplet at 5.65–5.68 ppm). It is interesting to note that a small long-range five-bond interaction is observed between the b and c/d protons in the COSY spectra of both isomers, which also contributes to the complexity of the corresponding signals.

The stereochemistry of **2a** and **2b** was clarified by NOE-difference experiments. In both isomers, the

vinylic protons c and d, which appear as four partially overlapped doublets at 5.03–5.12 ppm, gave a NOE with protons f and g (multiplets at 2.35–2.52 ppm), but not with proton b. Also in both isomers, proton b gives a NOE with proton a. This clearly indicates that both isomers exist preferentially as *s-trans* conformers. Furthermore, NOE experiments supplied additional evidence for the proposed structures: as expected, a strong correlation between protons b and e is observed for **2a**, but not for **2b**.

Thus, under the conditions used, myrcene undergoes an intramolecular oxidative cyclization combined with nucleophilic addition which leads to products with cyclopentane structure (Scheme 1). This novel reaction is catalyzed by palladium and dioxygen is involved as a final oxidant. As far as we know compounds **2** and **3** have not been described before.

The results on the palladium catalyzed myrcene oxidation in acetic acid are presented in Table 3. Along with major acetates **2a** and **2b**, one of the corresponding chlorides **3b**, whose ^1H -NMR spectrum is similar to that of **2b**, has also been detected in appreciable amounts (ca. 25%, runs 1–4). Its mass spectrum is also very similar to that of **2b** and shows two molecular ion peaks at: $m/e = 172$ and 170 with the relative

Table 3
Palladium catalyzed oxidation of myrcene^a

Run	Myrcene (mol l ⁻¹)	Temperature (°C)	Time (min)	Conversion ^b (%)	<i>S</i> _{ox} ^c (%)	Product distribution ^b (%)				
						2a/2b	3b	4	Isomers ^d	Others ^e
1	0.25	30	90	67	81	58	23	5	10	4
			140	85	77	58	19	5	8	10
2	0.25	40	45	56	90	66	24	–	8	2
			110	90	82	60	22	5	8	5
3	0.50	30	320	52	84	69	15	7	5	4
4	0.50	40	135	54	77	63	14	9	10	4
5 ^f	0.50	60	90	<5	0	–	–	–	~50	~50
6	0.25	50	15	40	90	63	27	–	5	5
			65	90	66	50	16	6	9	19
7	0.25	70	30	88	54	44	10	8	16	22
8	0.50	60	60	48	46	40	6	11	7	36
9 ^g	0.50	40	30	90	45	23	22	11	22	22

^a Conditions: [PdCl₂] = 0.02 mol l⁻¹, [CuCl₂] = 0.05 mol l⁻¹, [LiCl] = 0.17 mol l⁻¹, 1 MPa (O₂), solvent: HOAc.

^b Determined by GC and based on reacted myrcene.

^c Selectivity for the oxidation products **2** and **3**.

^d Isomers of myrcene.

^e Mainly oligomers of myrcene and unidentified products of further oxidation of **2** and **3**.

^f In the absence of PdCl₂.

^g [CuCl₂] = 0.02 mol l⁻¹, [LiCl] = 0.57 mol l⁻¹.

intensities of 1 and 3, respectively, clearly indicating the presence of chlorine in the molecule. Furthermore, the peak at $m/e = 134$, corresponding to the loss of hydrogen chloride, is also observed. At 30–40 °C, the combined selectivity for the five-membered oxidation products **2** and **3** reaches 80–90% on reacted myrcene (runs 1–4) at rather high conversions. In each run, this selectivity decreases at longer reaction times because of the further oxidation of dienes **2** and **3** and the total amounts of the consumed dioxygen becomes higher than stoichiometric amounts with respect to myrcene converted to **2** and **3** (Scheme 1).

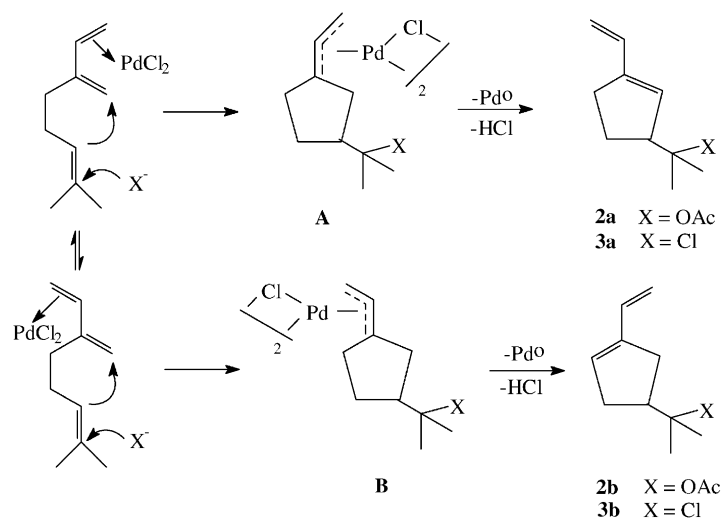
As expected, under the reaction conditions, myrcene undergoes both double bond and skeletal isomerization giving rise to ocimene and limonene, respectively. Limonene isomerizes further yielding terpinolene, α -terpinene and γ -terpinene. When significant isomerization occurs (run 9), the product of the palladium catalyzed allylic oxidation of limonene, i.e., carveyl acetate, is detected [3]. In addition, the reaction is complicated by myrcene oligomerization, whose contribution increases at higher temperatures. It is worthwhile to note the formation of product **4** with a GC retention time close to those of myrcene isomers (molecular weights of 136), but showing the molecular ion peak at $m/e = 134$. Its fragmentations are very similar to those of dienes **2** and **3**, thus it seems to be the product of oxidative cyclization of myrcene with a cyclopentane framework. Due to the difficulty of separation and its small concentration in the crude product, the structure of **4** has not been yet clarified completely.

In the absence of PdCl₂, no oxidation products **2–4** are formed, only slow isomerization and oligomerization of myrcene occur (run 5). The balance between the concomitant reaction pathways depends on the reaction conditions. In an attempt to accelerate the process, we varied some reaction parameters. The temperature effect could be clarified by comparing results within two sets of runs: 1, 2, 6 and 7 ([myrcene] = 0.25 mol l⁻¹) and 3, 4 and 8 ([myrcene] = 0.50 mol l⁻¹). The combined selectivity for **2** and **3**, at ca. 50% conversion, gradually decreases with increasing temperature: 84% at 30 °C (run 3), 77% at 40 °C (run 4) and 46% at 60 °C (run 8), mainly due to the formation of high-boiling products. Increasing temperature to 50 °C benefits the reaction rate, with a 40% conversion of myrcene being attained for 15 min and the selectivity remaining as

high as 90% (run 6). Then, the selectivity decreases markedly (66% at 90% conversion) because of the further oxidation of the primarily formed products. At 60–70 °C (runs 6 and 7), the contribution of this oxidation rises significantly and a total dioxygen uptake becomes higher than 0.5 mol per mole of reacted myrcene (Scheme 1), indicating the formation of polyoxygenated products. The concentration of product **2** passes a maximum, after which it slowly declines. Also, at higher temperatures the process seems to be more complicated by myrcene oligomerization. At 60–70 °C, the total amounts of high-boiling products reach 20–40% of reacted myrcene. It is worth noting that LiCl should be used in a lowest possible concentration, not higher than necessary to dissolve palladium and copper chlorides, because of its undesirable effect on the reaction selectivity and on the relative amounts of chlorinated product **3** (run 9).

The best result, in terms of catalyst activity and selectivity, was achieved at low temperature and relatively low substrate concentrations, when the oligomerization of myrcene is minimized (run 2). The selectivity for the oxidation products **2** and **3** reaches 90% at 56% conversion and 82% at 90% conversion, with very small amounts of high-boiling products being formed (2–5%).

The proposed pathway of myrcene oxidative cyclization is shown in Scheme 2. First, the π -allyl complexes **A** and **B** seem to be formed from *s-cis* and *s-trans* conformations of myrcene, respectively. It has been previously reported [16] that myrcene on treatment with disodium tetrachloropalladate(II) undergoes cyclization to the cyclopentane metal complex similar to those depicted in Scheme 2 (X = OMe in methanol and OH in acetone), rather than the alternative acyclic or cyclohexane metal complexes. Similar (π -allyl)-palladium complexes have been also described in [17,18]. The preference for five- over six-membered ring formation in electrophilic, free radical and photochemical cyclizations of myrcene has precedent [1] and may explain the course of reaction. Under the conditions employed, (π -allyl)-palladium intermediates decompose via a β -hydrogen rearrangement giving two isomers of substituted vinylcyclopentenes **2a** and **2b** (**3b**) and a palladium(II) hydride. The latter undergoes intramolecular redox reaction resulting in a proton and Pd(0) complex, which is recycled by CuCl₂. The re-



Scheme 2.

duced Cu(I) species are readily oxidized back to Cu(II) by dioxygen, thus completing the catalytic cycle.

The specific function of CuCl₂ in the oxidation of myrcene has been further confirmed by reactions, in which other reoxidants for palladium have been used. Although nitrate ions readily oxidize the reduced palladium species in acetic acid solutions and are reoxidized back by dioxygen, neither the significant oxygen consumption nor the formation of oxidation products are observed, in the presence of the Pd(OAc)₂ (0.08 equiv.)–LiNO₃ (1.6 equiv.) and Pd(OAc)₂ (0.08 equiv.)–Cu(NO₃)₂ (0.6 equiv.) combinations (25–45 °C). A similar result has been obtained using benzoquinone (Pd(OAc)₂, 0.04 equiv.; benzoquinone, 0.4 equiv.; 25–45 °C) as reoxidant for palladium. These observations indicate that CuCl₂ has behavior far exceeding that of a simple reoxidation agent. We suppose that one of the specific functions of CuCl₂ is to assist at the decomposition of the (π-allyl)–palladium intermediate due to the formation of the bridging Pd–Cl–Cu complexes analogous to those reported in our previous publication [27]. It is worthwhile noting that earlier [3] we obtained similar results studying the oxidation of limonene: the PdCl₂–CuCl₂ system effectively catalyzed the allylic oxidation of limonene by dioxygen, while the Pd(OAc)₂–LiNO₃ system was almost completely inactive. We are presently working on optimization of

this novel catalytic reaction and studying its mechanism.

4. Conclusions

In summary, a novel selective PdCl₂–CuCl₂ catalyzed oxidation of myrcene, which is readily available natural raw material, by dioxygen has been developed. The reaction results in new functionalized monoterpenes with cyclopentane skeleton, which have a pleasant scent with a flower or fruit tinge and could be used as components of synthetic perfumes.

Acknowledgements

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