

Synthesis of fragrance compounds from acyclic monoterpenes: Rhodium catalyzed hydroformylation and tandem hydroformylation/acetalization of linalool and β -citronellene

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ABSTRACT

Rhodium-catalyzed hydroformylation of acyclic monoterpenic compounds, i.e., linalool and β -citronellene, was studied in toluene and ethanol solutions in the presence of PPh_3 or $\text{P}(\text{O}-o\text{-}^i\text{BuPh})_3$ ligands. Although both substrates have a monosubstituted terminal double bond, they show different behavior under the hydroformylation conditions. In toluene, linalool gave almost quantitatively a cyclic hemiacetal; whereas the hydroformylation of β -citronellene resulted in two isomeric aldehydes also in a nearly quantitative combined yield. The reactions occurred approximately two times faster in ethanol than in toluene giving the corresponding acetals even in the absence of additional acid co-catalysts. In the absence of phosphorous ligands, linalool (differently from β -citronellene) was very resistant to hydroformylation probably due to the binding with rhodium through both the double bond and the hydroxyl group to form stable chelates. The $\text{P}(\text{O}-o\text{-}^i\text{BuPh})_3$ ligand exerted a remarkable effect on the reactivity of both substrates accelerating the reactions by 5–20 times as compared to the system with PPh_3 . Several fragrance compounds were obtained in high yields through a simple one-pot procedure starting from the substrates easily available from natural bio-renewable resources.

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1. Introduction

Terpenic compounds, in general, are an important biomass-based renewable feedstock for the industrial production of fragrances, perfumes, flavors and pharmaceuticals as well as synthetic intermediates [1–4]. These natural compounds are easily available from essential oils of many plants and flowers. For several years, we have been interested in catalytic transformations of terpenes to more valuable chemicals, in particular, via hydroformylation reactions [5–9]. Rhodium or cobalt catalyzed hydroformylation is an industrially important tool for the synthesis of oxygen-containing compounds from alkenes [10]. The process is usually performed in aprotic solvents and gives aldehydes as main products, which can be further converted to other desired compounds.

Although the hydroformylation of more abundant monoterpenes, such as limonene, β -pinene, myrcene and camphene, was quite extensively studied [11–20], only few reports appeared on the hydroformylation of linalool [11,21–23] and β -citronellene (dihydromyrcene) [11,24,25]. Linalool, a monoterpenoid allylic alcohol with a pleasant lily odor, is a key building block for the

synthesis of various vitamins and fragrances, such as vitamin A, vitamin E, citral and citronellol [3,4]. Linalool is found in essential oils of several plants, e.g., Brazilian rosewood and Chinese Ho leaf oils, but most linalool is produced synthetically from α -pinene, a cheap major constituent of turpentine oils obtained from coniferous trees [3,4,26]. The hydroformylation of allylic alcohols represents a direct method for the synthesis of substituted tetrahydrofurans since primarily formed hydroxyl-aldehydes undergo a spontaneous intramolecular cyclization to give five-membered hemiacetals [13,27–30]. Hemiacetals can be further converted in other useful products: acetals, lactones or dihydrofuran derivatives.

β -Citronellene is also a valuable feedstock for the industrial synthesis of various fragrance ingredients, e.g., dihydromyrcenol and cyclodol [3]. β -Citronellene is commercially produced by the thermal isomerization of pinane obtained through the hydrogenation of α -pinene [3,31,32]. α -Pinene is one of the most widespread monoterpene hydrocarbons; its content in turpentine oils can reach 85%. Aldehydes and acetals resulting from the hydroformylation of β -citronellene and linalool are valuable fragrance compounds with fresh floral and/or green citrus odors [11].

Following a general trend in synthetic organic chemistry, we have recently directed our efforts to involve the hydroformylation reaction in tandem reaction sequences [8,9,33,34]. Such catalytic processes can lead directly from alkenes to various important products through a simple one-pot procedure without the isolation of

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aldehydes. In particular, we integrated the hydroformylation and aldehyde acetalization steps in one reactor by performing the process in ethanol solutions, which allowed to obtain diethyl acetals from various monoterpenes [9,35].

In continuation of our ongoing project on valorization of natural ingredients of essential oils, we report herein the rhodium-catalyzed hydroformylation of linalool (**1a**) and β -citronellene (**2a**) as well as the tandem hydroformylation/acetalization of these substrates under mild non-acidic conditions. All isolated products (aldehydes, hemiacetals and acetals) have a pleasant scent and can be useful as components of synthetic fragrances.

2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. Racemic linalool [($\pm$)-3,7-dimethyl-1,6-octadien-3-ol] and (–)- β -citronellene [dihydromyrcene, (R)-(–)-3,7-dimethyl-1,6-octadiene] acquired from Aldrich were used as substrates. $[\text{Rh}(\text{COD})(\text{OMe})_2]$ (COD=1,5-cyclooctadiene) was prepared by a published method [36]. Tris(*O*-^{*t*}-butylphenyl)phosphite, $\text{P}(\text{O}-\text{o}^{\text{t}}\text{BuPh})_3$, was prepared as described in [37] and purified by column chromatography (silica gel 60) using mixture of hexane and CHCl_3 as eluents. Toluene was purified under reflux with sodium wire–benzophenone for 8 h and then distilled under argon. Ethanol was purified under reflux with magnesium turnings and iodine crystals for 6 h and then distilled under argon.

Catalytic experiments were carried out in homemade stainless steel reactors with magnetic stirring. Reactions were followed by gas chromatography (GC) by sampling the liquid phases through a valved dip tube. The products were analyzed by gas chromatography (GC–Shimadzu QP2010, Rtx®-5MS capillary column, FID detector). Conversion and selectivity were determined by GC. The GC mass balance was based on the substrate charged using dodecane as an internal standard. Initial turnover frequencies (TOFs) were measured at low conversions (up to 20–40%) taking aliquots at short reaction times for GC analysis.

In a typical run, toluene or ethanol (20.0 mL) containing $[\text{Rh}(\text{COD})(\text{OMe})_2]$ (5.0–6.0 μmol), phosphorus ligand (0–0.6 mmol), substrate (2–6 mmol), and dodecane (1–3 mmol, internal standard) was transferred under argon into a stainless steel autoclave, which was pressurized to 20–80 atm ($\text{CO}/\text{H}_2 = 1/2$ to $2/1$), placed in an oil bath (40–80 °C), and magnetically stirred. After the reaction was carried out and cooled to room temperature, the excess CO and H_2 were slowly vented.

The products were separated by column chromatography (silica gel 60) using mixtures of hexane and CH_2Cl_2 as eluents and identified by GC–MS, ^1H , and ^{13}C NMR. The assignment of ^1H and ^{13}C NMR signals was made using bidimensional techniques. NMR spectra were recorded in CDCl_3 using a Bruker 400 MHz spectrometer, with TMS as an internal standard. Mass spectra were obtained on a Shimadzu QP2010-PLUS instrument operating at 70 eV.

For the NMR and MS data *cis*-5-methyl-5-(4-methyl-3-pentenyl)tetrahydro-2-furanol (**1c cis** and *trans*) see [23].

Data for 4,8-dimethyl-7(8)-nonenal (2b**):** MS (70 eV, EI): m/z (%): 168 (2) [M^+], 135 (26), 109 (55), 107 (20), 81 (26), 70 (20), 69 (100), 67 (27), 56 (21), 55 (45). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 0.89 (d, 3J = 6.4 Hz, 3H; C^{10}H_3), 1.12–1.22 (m, 1H; C^4HH), 1.28–1.38 (m, 1H; C^4HH), 1.40–1.50 (m, 2H; C^3H and C^2HH), 1.60 (s, 3H; C^8H_3), 1.68 (s, 3H; C^9H_3), 1.65–1.75 (m, 1H; C^2HH), 1.90–2.05 (m, 2H; C^5H_2), 2.38–2.48 (m, 2H; C^1H_2), 5.09 (t, 3J = 7.0 Hz, 1H; C^6H), 9.77 ppm (t, 3J = 1.8 Hz, 1H; CHO). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ_{C} = 17.61 (C^8), 19.21 (C^{10}), 25.41 (C^5), 25.67 (C^9), 28.83 (C^2), 32.00 (C^3), 36.73 (C^4), 41.66 (C^1), 124.51 (C^6), 131.37 (C^7), 202.89 ppm (CHO).

Data for 2,3,7-trimethyl-6(7)-octenal (2c**,** a mixture of two diastereoisomers: (2R,3R) and (2S,3R), shorter GC retention time compared to **2b**): MS (70 eV, EI): m/z (%): 168 (2) [M^+], 135 (19), 109 (43), 95 (76), 85 (21), 83 (34), 82 (32), 70 (25), 69 (100), 67 (43), 56 (26), 55 (57). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 0.83 and 0.98 (d, 3J = 7.0 Hz, 3H; C^1H_3), 0.89 (d, 3J = 6.4 Hz, 3H; C^{10}H_3), 1.12–1.22 (m, 1H; C^4HH), 1.28–1.38 (m, 1H; C^4HH), 1.40–1.50 (m, 2H; C^3H), 1.60 (s, 3H; C^8H_3), 1.68 (s, 3H; C^9H_3), 1.90–2.05 (m, 2H; C^5H_2), 2.25–2.35 (m, 1H; C^2H), 5.09 (t, 3J = 7.0 Hz, 1H; C^6H), 9.68 and 9.67 ppm (br. s, 1H; CHO). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ_{C} = 14.07 and 15.34 (C^1), 17.27 (C^8), 19.20 (C^{10}), 25.63 (C^5), 25.67 (C^9), 32.15 and 33.40 (C^3), 33.25 and 34.74 (C^4), 50.51 and 51.50 (C^2), 123.98 and 124.06 (C^6), 131.78 and 131.80 (C^7), 205.64 and 205.70 ppm (CHO).

Data for *cis*-5-ethoxy-2-methyl-2-(4-methyl-3-pentenyl)tetrahydrofuran (*cis*) (1d cis**):** MS (70 eV, EI): m/z (%): 212 (0.5) [M^+], 166 (15) [$\text{M}^+ - \text{C}_2\text{H}_5\text{OH}$], 129 (79), 123 (20), 122 (54), 109 (26), 108 (12), 107 (55), 101 (39), 95 (25), 86 (27), 85 (22), 83 (56), 69 (100), 67 (20), 58 (22), 55 (35). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.15–1.25 (m, 3H; CH_2CH_3), 1.33 (s, 3H; C^{10}H_3), 1.40–1.50 (m, 2H; C^4H_2), 1.61 (s, 3H; C^8H_3), 1.67 (s, 3H; C^9H_3), 1.75–1.90 (m, 2H; C^2H_2), 1.90–2.00 (m, 4H; C^5H_2 and C^1H_2), 3.35–3.45 (m, 1H; CHHCH_3), 3.70–3.80 (m, 1H; CHHCH_3), 5.05–5.15 ppm (m, 2H; C^6H and OCHOC_2H_5). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ_{C} = 15.21 (CH_2CH_3), 17.55 (C^8), 23.23 (C^5), 25.42 (C^9), 28.24 (C^{10}), 33.29 (C^1), 34.36 (C^2), 41.91 (C^4), 61.99 (CH_2CH_3), 84.17 (C^3), 103.83 (OCHOC_2H_5), 124.45 (C^6), 131.27 ppm (C^7).

Data for *trans*-5-ethoxy-2-methyl-2-(4-methyl-3-pentenyl)tetrahydrofuran (*trans*) (1d trans**,** shorter GC retention time compared to **1d cis**): MS (70 eV, EI): m/z (%): 212 (0.2) [M^+], 166 (23) [$\text{M}^+ - \text{C}_2\text{H}_5\text{OH}$], 129 (73), 123 (27), 122 (80), 109 (32), 108 (20), 107 (84), 101 (37), 95 (27), 86 (22), 85 (21), 83 (57), 69 (100), 67 (25), 58 (20), 55 (38). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.15–1.25 (m, 3H; CH_2CH_3), 1.33 (s, 3H; C^{10}H_3), 1.62 (s, 3H; C^8H_3), 1.67 (s, 3H; C^9H_3), 1.65–1.70 (m, 2H; C^4H_2), 1.90–2.00 (m, 6H; C^2H_2 , C^5H_2 and C^1H_2), 3.35–3.45 (m, 1H; CHHCH_3), 3.70–3.80 (m, 1H; CHHCH_3), 5.05–5.15 ppm (m, 2H; C^6H and OCHOC_2H_5). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ_{C} = 15.13 (CH_2CH_3), 17.49 (C^8), 23.57 (C^5), 26.07 (C^9), 28.24 (C^{10}), 32.69 (C^1), 34.77 (C^2), 42.78 (C^4), 62.10 (CH_2CH_3), 84.45 (C^3), 103.57 (OCHOC_2H_5), 124.65 (C^6), 131.10 ppm (C^7).

Data for 9,9-diethoxy-2,6-dimethylnon-2-ene (2d**):** MS (70 eV, EI): m/z (%): 196 (6) [$\text{M}^+ - \text{C}_2\text{H}_5\text{OH}$], 135 (20), 109 (29), 107 (22), 103 (100), 97 (20), 96 (29), 95 (51), 85 (28), 81 (41), 75 (84), 69 (55), 57 (31). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 0.85 (d, 3J = 6.4 Hz, 3H; C^{10}H_3), 1.18 (t, 3J = 6.8 Hz, 6H; CH_2CH_3), 1.10–1.20 (m, 2H; C^4HH and C^2HH), 1.25–1.45 (m, 3H; C^4HH , C^2HH and C^3H), 1.57 (s, 3H; C^8H_3), 1.50–1.65 (m, 2H; C^1H_2), 1.65 (s, 3H; C^9H_3), 1.85–2.05 (m, 2H; C^5H_2), 3.40–3.50 (m, 2H; CHHCH_3), 3.55–3.65 (m, 2H; CHHCH_3), 4.43 (t, 3J = 6.0 Hz, 1H; $\text{CH}(\text{OC}_2\text{H}_5)$), 5.07 ppm (t, 3J = 7.2 Hz, 1H; C^6H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ_{C} = 15.38 (CH_2CH_3), 17.54 (C^8), 19.42 (C^{10}), 25.46 (C^5), 25.62 (C^9), 31.02 (C^1), 31.63 (C^2), 32.22 (C^3), 36.91 (C^4), 60.67 (CH_2CH_3), 60.74 (CH_2CH_3), 103.28 ($\text{CH}(\text{OC}_2\text{H}_5)$), 124.90 (C^6), 131.04 ppm (C^7).

Data for 8,8-diethoxy-2,6,7-trimethyloct-2-ene (2e**,** shorter GC retention time compared to **2d**): MS (70 eV, EI): m/z (%): 196 (2) [$\text{M}^+ - \text{C}_2\text{H}_5\text{OH}$], 135 (19), 103 (100), 95 (35), 75 (83), 69 (23).

3. Results and discussion

We have studied the behavior of linalool (**1a**) and β -citronellene (**2a**) under the hydroformylation conditions in toluene and ethanol solutions using $[\text{Rh}(\text{COD})(\text{OMe})_2]$ as a catalyst precursor in the presence of PPh_3 or tris(*O*-^{*t*}-butylphenyl)phosphite, $\text{P}(\text{O}-\text{o}^{\text{t}}\text{BuPh})_3$,

Table 1
Rhodium catalyzed hydroformylation of linalool (**1a**).^a

Run	Ligand	P/Rh	Time (h)	Conversion (%)	TOF (h ⁻¹)	Selectivity for 1c (%) (<i>cis/trans</i>)
1 ^b	PPh ₃	10	6.0	100	38	94 (93/7)
2 ^{b,c}	P(O- <i>o</i> - ^t BuPh) ₃	10	0.5	96	385	87 (92/8)
3 ^d	P(O- <i>o</i> - ^t BuPh) ₃	10	1.5	100	400	98 (89/11)
4 ^d	P(O- <i>o</i> - ^t BuPh) ₃	20	2.0	99	233	99 (87/13)
5 ^d	P(O- <i>o</i> - ^t BuPh) ₃	50	3.0	100	183	99 (85/15)
6 ^d	P(O- <i>o</i> - ^t BuPh) ₃	5	1.5	98	350	99 (91/10)
7 ^d	P(O- <i>o</i> - ^t BuPh) ₃	1	1.5	94	300	91 (94/6)
8 ^{d,e}	None	–	6.0	12	10	85 (30/70)
9 ^d	PPh ₃	5	21.0	47	33	89 (20/80)

^a For most of the runs the reaction time is given for nearly complete conversions. Conversion and selectivity are based on the substrate reacted. TOF – initial turnover frequency (mol of the substrate converted per mol of Rh per hour).

^b Conditions: linalool (0.10 M), [Rh(COD)(OMe)]₂ (0.25 mM), ligand (5.0 mM), 50 °C, 80 atm (CO/H₂ = 1/1), toluene.

^c Average TOF is given as the reaction was too fast.

^d Conditions: linalool (0.30 M), [Rh(COD)(OMe)]₂ (0.30 mM), 40 °C, 20 atm (CO/H₂ = 1/1), toluene.

^e 50 °C.

as P-donor auxiliary ligands. The hydroformylation of linalool in toluene with the Rh/PPh₃ system has been described in our previous publication [23]; however, we have included some runs in the tables for comparison.

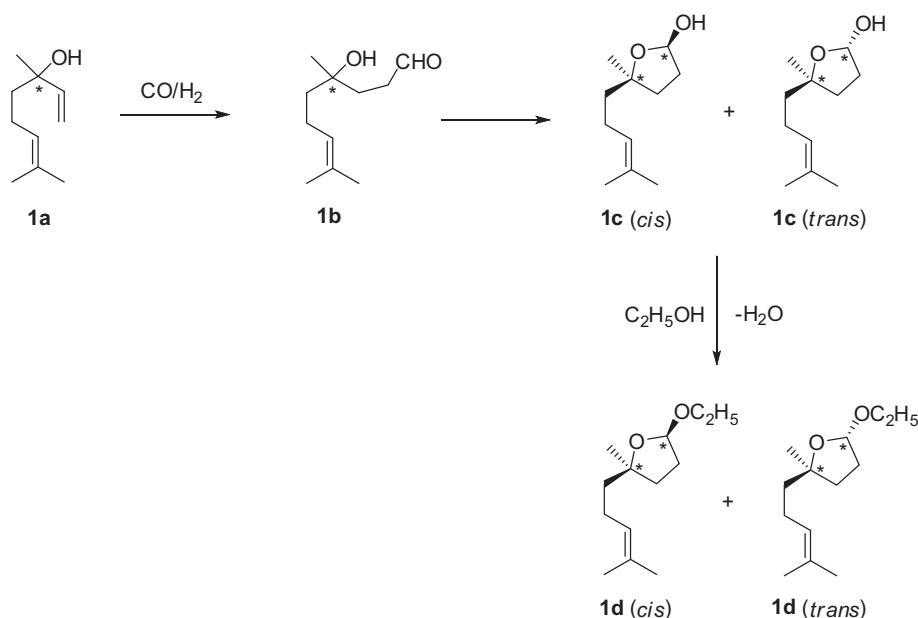
Under the hydroformylation conditions in toluene, both substrates gave one or two major products derived from the direct carbonylation of their terminal double bonds. No reactivity of the internal double bond was observed even in the system with the bulky P(O-*o*-^tBuPh)₃ ligand. When the reactions were performed in ethanol, the corresponding acetals appeared in the reaction mixtures due to the in situ acetalization of the primarily formed products. It is important to point out that the formation of acetals occurred without using any additional acid co-catalyst. The regio- and stereoselectivity of the reaction steps was remarkably dependent on the reaction variables and the nature of the auxiliary phosphorous ligand. The substrates and corresponding products are numbered in the present communication by the same number with the addition of the letter “a” to indicate the substrate and other letters to indicate the products derived from this substrate. In all products, we have maintained a carbon numbering conventionally used for starting monoterpene molecules. The total selectivity for the hydroformylation products in most of the runs exceeded 95%

for both substrates, with GC yields for some individual products being nearly quantitative under optimized conditions.

3.1. Hydroformylation of linalool in toluene solutions

Hydroformylation of linalool in the presence of PPh₃ gave hemiacetal **1c** as the main product (Table 1, run 1, Scheme 1). This product formally results from the intramolecular cyclization of the primarily formed hydroxy aldehyde **1b**, which we have never detected in the reaction solutions. Hemiacetal was formed almost exclusively with a *cis* configuration of the methylpentenyl and hydroxyl groups with respect to the tetrahydrofuran ring. The use of the P(O-*o*-^tBuPh)₃ ligand instead of PPh₃ remarkably increased the reactivity of linalool (Table 1, run 2 vs. run 1). The reaction in run 2 was too fast for measuring the initial rate by GC being completed for 30 min. However, even the average turnover frequency (TOF) in the run with P(O-*o*-^tBuPh)₃ was more than ten times higher than the initial TOF in the reaction performed with PPh₃ under the same conditions. In a further study we decreased the temperature and the pressure to slow down the reactions.

The hydroformylation of linalool with the Rh/P(O-*o*-^tBuPh)₃ system at 40 °C and 20 atm resulted in nearly quantitative yield of



Scheme 1. Hydroformylation/acetalization of linalool (**1a**).

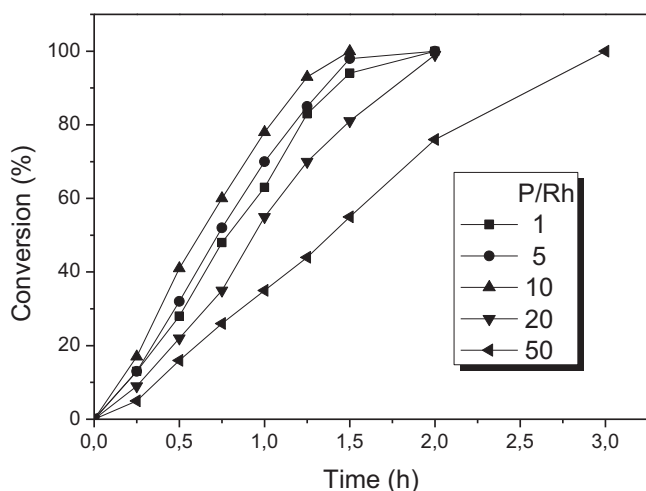


Fig. 1. Hydroformylation of linalool catalyzed by Rh/P(O-*o*-*t*-BuPh)₃: effect of the P/Rh ratio. Conditions: linalool (0.30 M), [Rh(COD)(OMe)]₂ (0.30 mM), 40 °C, 20 atm (CO/H₂ = 1/1), toluene.

hemiacetal **1c** (ca. 90% *cis*, Table 1, runs 3–5). Kinetic curves for the runs with various P/Rh ratios (runs 2–7 in Table 1) are presented in Fig. 1. A slight acceleration can be seen when the P/Rh ratio increases from 1 to 10, whereas further addition of the ligand decreases the reaction rate. The kinetic curves are nearly straight lines up to 80–90% conversions even at P/Rh = 50, indicating that the substrate competes successfully with the ligand for the coordination sites on rhodium. In other words, the substrate reacts with rhodium quite readily and a majority of the metal centers, even at high conversions and high ligand concentrations, contain strongly coordinated linalool or fragments derived from linalool. In most of the runs, the *cis* isomer of **1c** predominated (85–95%), with its relative amounts being only slightly decreased with the increase in the ligand concentration.

An unexpected accelerating effect of PPh₃ on the reactivity of linalool has been reported in our previous publication [23]. In the present work, we have found that the acceleration is much more pronounced with the P(O-*o*-*t*-BuPh)₃ ligand. In the absence of the P ligand, only a 12% conversion was observed for 6 h, while with small amounts of P(O-*o*-*t*-BuPh)₃ the reaction was nearly completed in 1.5 h even at lower temperature (cf. runs 7 and 8, Table 1). In most modified rhodium systems, the hydroformylation rate decreases with the increase in the P-ligand concentration due to the competition between the ligand and the substrate for coordination sites on rhodium. The unusual effect observed at the hydroformylation of linalool can be explained by the chelation of the substrate on rhodium through the coordination of both the double bond and the hydroxyl group [23]. The increase in the P-ligand concentration favors the cleavage of the inactive chelates allowing the proper positioning of the C–C double bond for the hydride migration. It is remarkable that the presence of only 0.2 mol% of P(O-*o*-*t*-BuPh)₃ (P/Rh = 1) is sufficient to overcome the chelation problem and to perform the hydroformylation of linalool rapidly (TOF = 300 h^{−1}) and selectively under mild conditions (Table 1, run 7).

The strong effect of the ligand nature on the hydroformylation of linalool is illustrated in Fig. 2, which shows the kinetic curves for the reactions with PPh₃ and P(O-*o*-*t*-BuPh)₃ under the same conditions (Table 1, runs 6 and 9). Only 20% of linalool was converted for 8 h in the presence of PPh₃, with the 3-h induction period being observed on the reaction profile. Nevertheless, the reaction in the presence of P(O-*o*-*t*-BuPh)₃ occurred more than ten times faster without any induction period (TOF = 350 vs. 33). The existence of the induction

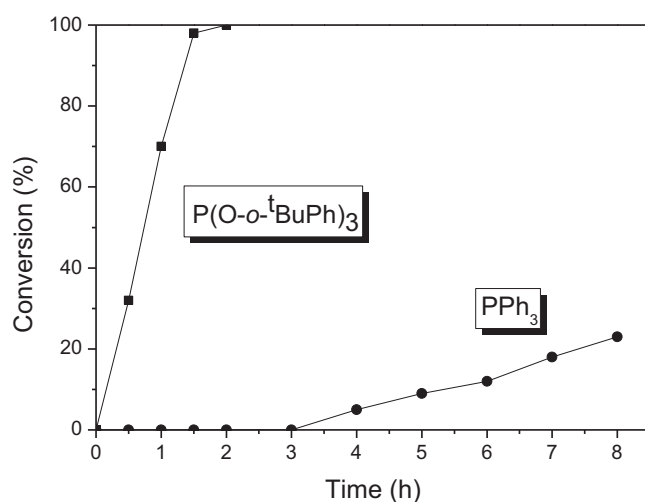


Fig. 2. Rhodium catalyzed hydroformylation of linalool: ligand effect. Conditions: linalool (0.30 M), [Rh(COD)(OMe)]₂ (0.30 mM), ligand (3.0 mM), 40 °C, 20 atm (CO/H₂ = 1/1), toluene.

period in the Rh/PPh₃ system supports the chelation hypothesis: at the beginning of the reaction, inactive rhodium–linalool chelate complexes should be opened by the PPh₃ coordination [23]. A great advantage of using P(O-*o*-*t*-BuPh)₃ consists in a high efficiency of this ligand to prevent the linalool chelation and/or to break up rhodium–linalool chelates. Even in the reaction with small amounts of P(O-*o*-*t*-BuPh)₃, no induction period was observed on the kinetic curves.

The effect of the ligand nature on the stereochemistry of the hemiacetal deserves a special attention. On changing the ligand from P(O-*o*-*t*-BuPh)₃ to PPh₃ under the same reaction conditions, the stereoselectivity of cyclization was virtually switched from *cis* to *trans* (Table 1, runs 6 and 9). This result contradicts with the reaction path shown in Scheme 1, in which two reaction steps occur consecutively with no participation of rhodium in the cyclization step. A spontaneous cyclization of aldehyde **1b** should give preferably the thermodynamically more stable *trans* isomer of **1c** and stereochemistry should not depend on the ligands on the rhodium species. A strong ligand effect argues for the suggestion that the interaction between the hydroxyl and carbonyl groups leading to the intramolecular cyclization could also occur in the rhodium acyl intermediate before its hydrogenolysis to give aldehyde **1b** [23]. The cyclization of the rhodium acyl intermediate should give preferably a less hindered cyclic rhodium intermediate in which a bulky rhodium/P(O-*o*-*t*-BuPh)₃ fragment and methylpentenyl group are at the opposite sides of the tetrahydrofuran ring. The hydrogenolysis of the *trans* cyclic rhodium intermediate will give hemiacetal **1c** with the methylpentenyl and hydroxyl groups in a *cis* position.

The inversion of stereochemistry of hemiacetal from *cis* to *trans* can also be achieved by the increase in the hydrogen pressure as higher hydrogen concentrations favor the hydrogenolysis of the rhodium acyl intermediate before its cyclization. At 20 atm (CO/H₂ = 1/1), the *cis* isomer accounted for ca. 90% of the mass balance; whereas at 80 atm, both isomers were formed in comparable amounts (Table 2, run 1 vs. run 3). Moreover, increasing only the hydrogen pressure allowed to obtain the *trans* isomer in nearly 80% yield (Table 2, run 4). On the other hand, the increase in the reaction temperature switched stereoselectivity again to *cis* isomer (cf. run 3 in Table 2 and run 2 in Table 1). Thus, through the choice of reaction variables we can control stereochemistry of the hydroformylation product derived from linalool. Each of two isomers of hemiacetal **1c** can be obtained in 75–90% individual yields under appropriate conditions.

Table 2
Rhodium catalyzed hydroformylation of linalool (**1a**): effect of pressure^a

Run	P (CO) (atm)	P (H ₂) (atm)	TOF (h ⁻¹)	Selectivity for 1c (%) (cis/trans)
1	10	10	400	98 (89/11)
2	25	25	350	97 (86/14)
3	40	40	330	95 (42/58)
4 ^b	10	40	1830	96 (23/77)
5	40	10	100	97 (91/9)

^a Conditions: linalool (0.30 M), [Rh(COD)(OMe)]₂ (0.30 mM), P(O-*o*-^tBuPh)₃ (6.0 mM), P/Rh = 10, 40 °C, toluene. Selectivity at nearly complete conversions is given and is based on the substrate reacted. TOF – initial turnover frequency (mol of the substrate converted per mol of Rh per hour).

^b Average TOF is given as the reaction was too fast.

Table 3
Rhodium catalyzed hydroformylation of β-citronellene (**2a**).^a

Run	Ligand	P/Rh	P (CO) (atm)	P (H ₂) (atm)	Time (h)	TOF (h ⁻¹)	Selectivity (%)	
							2b	2c
1	PPh ₃	2	40	40	4.0	54	74	21
2	PPh ₃	10	40	40	7.0	42	84	15
3	PPh ₃	20	40	40	9.0	36	84	15
4	PPh ₃	40	40	40	10.0	34	84	15
5	PPh ₃	10	20	20	6.0	44	84	15
6	PPh ₃	10	40	20	9.0	26	83	16
7	PPh ₃	10	20	40	4.0	80	84	15
8	None	–	40	40	1.0	200	70	21
9	P(O- <i>o</i> - ^t BuPh) ₃	10	40	40	0.75	520	68	31
10	P(O- <i>o</i> - ^t BuPh) ₃	20	40	40	0.75	480	68	32
11 ^b	P(OPh) ₃	10	40	40	3.0	9	55	10

^a Conditions: β-citronellene (0.10 M), [Rh(COD)(OMe)]₂ (0.25 mM), 50 °C, toluene. Conversion and selectivity are based on the substrate reacted; the reaction time is given for nearly complete conversions. TOF – initial turnover frequency (mol of the substrate converted per mol of Rh per hour).

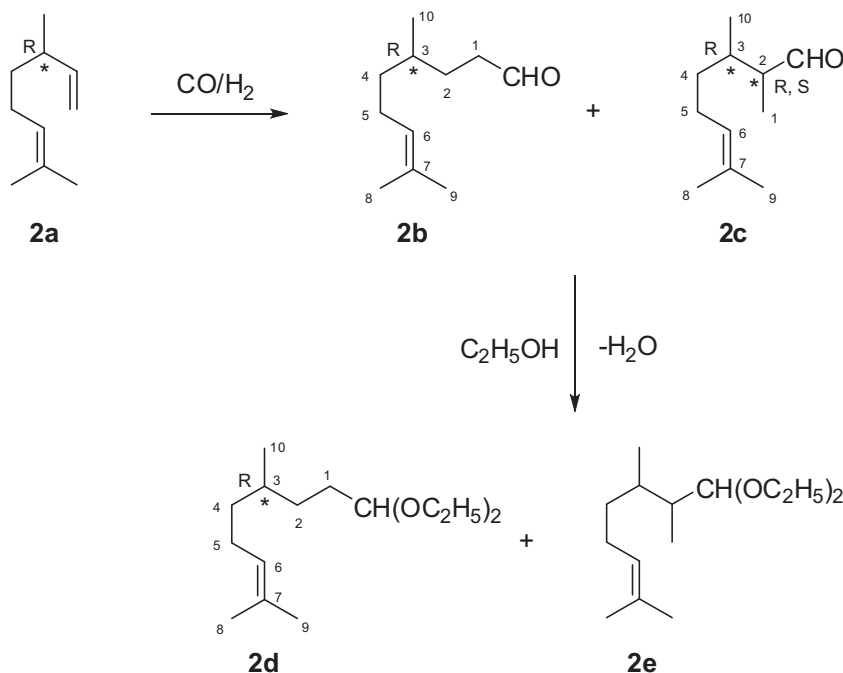
^b 14% conversion for 3 h.

A concerned to the effects of the carbon monoxide and hydrogen pressure on the hydroformylation of linalool in the Rh/P(O-*o*-^tBuPh)₃ system, the general trends are similar to those observed in the Rh/PPh₃ system [23]: a nearly first positive order in hydrogen and also nearly first negative order in carbon monoxide (Table 2). The increase in the total pressure decreased only slightly the reaction rates (Table 2, runs 1–3), reflecting a net result of the opposite kinetic effects of the gas reagents. The accelerating effect of hydrogen suggests that the oxidative addition of hydrogen to the

rhodium acyl intermediate seems to be a rate-determining step at the linalool hydroformylation.

3.2. Hydroformylation of β-citronellene in toluene solutions

The hydroformylation of β-citronellene (**2a**) occurred smoothly in toluene solutions in the presence of PPh₃, with selectivity being high even at low P/Rh ratio (Table 3, run 1). Two aldehydes resulted from the hydroformylation of the terminal double bond were

**Scheme 2.** Hydroformylation/acetalization of β-citronellene (**2a**).

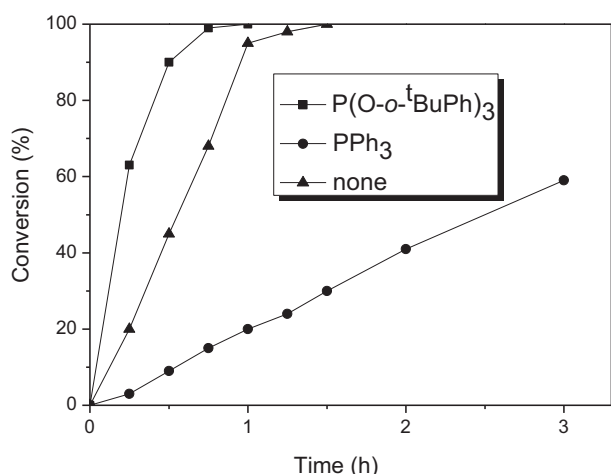


Fig. 3. Rhodium catalyzed hydroformylation of β -citronellene: ligand effect. Conditions: β -citronellene (0.10 M), $[\text{Rh}(\text{COD})(\text{OMe})_2]$ (0.25 mM), ligand (5.0 mM), 50 °C, 80 atm ($\text{CO}/\text{H}_2 = 1/1$), toluene.

formed with a 95% combined selectivity (Scheme 2), the linear isomer (**2b**) accounting for 74% of the mass balance. The branched aldehyde (**2c**) was formed as a mixture of two diastereoisomers, (2R,3R) and (2S,3R), detected in nearly equal amounts as the molecule of starting β -citronellene has R configuration at asymmetric carbon C-3. The diastereoisomers were not GC separable under the conditions used; however, their molecules showed different NMR spectra.

The increase in P/Rh to 10 expectedly decreased the reaction rate and improved selectivity for aldehydes, which were formed in a nearly quantitative combined yield. A further increase in the phosphine concentration did not affect significantly the reaction.

In the absence of the P-ligand, the hydroformylation of β -citronellene occurred faster than in the Rh/PPh₃ system, albeit with lower selectivity (Table 3, cf. run 8 and run 2). This result is expected for simple non-functionalized non-conjugated alkenes due to the competition between the phosphine and the substrate for the coordination sites on rhodium. On the other hand, a significant accelerating effect of the phosphite ligand, P(O-*o*-^tBuPh)₃, as compared to the unmodified system is much less expected. The reaction in the presence of P(O-*o*-^tBuPh)₃ was 2.5 times faster than in the absence of the P-ligand and more than ten times faster than with PPh₃ (Table 3, runs 2, 8 and 9; Fig. 3).

The accelerating effect of P(O-*o*-^tBuPh)₃ as compared to PPh₃ can be explained by the large cone angle of the former, which disfavors the formation of bis(phosphorous ligand) rhodium species. At the same P/Rh ratios, for the Rh/P(O-*o*-^tBuPh)₃ system a larger part of rhodium exists as mono(phosphorous ligand) species, which are more active in hydroformylation. Furthermore, the weaker σ -basicity combined with the stronger π -acidity of P(O-*o*-^tBuPh)₃ (χ -value of 30.50 vs. 13.25 for PPh₃) favors the more facile CO dissociation and the stronger alkene association with rhodium [38]. In the presence of phosphite, the initial reaction rates depended only slightly on the ligand concentration (Table 4, runs 1–3). Thus, the P/Rh ratio of 10 is enough to keep most of rhodium coordinated to one P(O-*o*-^tBuPh)₃ and, even at P/Rh = 30, bis(phosphorous ligand) species are not formed in appreciable amounts. On the other hand, the reaction with less bulky phosphite, P(OPh)₃, was much slower than that with P(O-*o*-^tBuPh)₃ (Table 3, run 11).

We have also studied the effects of the carbon monoxide and hydrogen pressure on the hydroformylation of β -citronellene (Tables 3 and 4). The general trends are similar for both ligands: a positive order in hydrogen (Table 3, cf. runs 2 and 6; Table 4, cf. runs 1 and 6) and an inverse order in carbon monoxide (Table 3, cf.

Table 4
Hydroformylation of β -citronellene (**2a**) catalyzed by Rh/P(O-*o*-^tBuPh)₃.^a

Run	P/Rh	P(CO) (atm)	P(H ₂) (atm)	Time (h)	TOF (h ⁻¹)	Selectivity (%)	
						2b	2c
1	10	40	40	1.5	240	68	31
2	20	40	40	1.5	200	66	33
3	30	40	40	1.5	240	66	33
4	10	20	20	1.5	250	68	31
5	10	20	40	0.75	360	67	32
6	10	40	20	2.0	150	66	32

^a Conditions: β -citronellene (0.10 M), $[\text{Rh}(\text{COD})(\text{OMe})_2]$ (0.25 mM), 40 °C, toluene. Conversion and selectivity are based on the substrate reacted; the reaction time is given for nearly complete conversions. TOF – initial turnover frequency (mol of the converted substrate per mol of Rh per hour).

runs 2 and 7; Table 4, cf. runs 1 and 5). The variation in the total pressure of the equimolar gas mixture had no influence on the reaction rates due to the opposite kinetic effects of the gas reagents (Table 3, cf. runs 2 and 5; Table 4, cf. runs 1 and 4). The positive order in hydrogen observed at relatively high pressures suggests that the hydrogenolysis of the rhodium acyl intermediate seems to be the most likely rate-determining step in the hydroformylation of β -citronellene.

The results of the kinetic study are in agreement with the observed accelerating effect of P(O-*o*-^tBuPh)₃ in the hydroformylation of β -citronellene as compared to the unmodified system. It is reasonable to expect that a higher steric hindrance in the active rhodium species containing the bulky P(O-*o*-^tBuPh)₃ ligand will result in lower reaction rates. However, the reaction occurs much faster in the presence of P(O-*o*-^tBuPh)₃ implying that electronic rather than steric parameters dominate in this system. Considering that P(O-*o*-^tBuPh)₃ is more basic ligand than CO, the rhodium center should be more electron rich as compared to the center with only carbonyl ligands. Therefore, the most likely rate-determining step which involves the oxidative addition of hydrogen should be accelerated by the presence of the phosphite ligand on rhodium. It is also important that in the Rh/P(O-*o*-^tBuPh)₃ system (differently from the Rh/PPh₃ system) the formation of less active bis(phosphorous ligand) rhodium species is highly disfavored by the ligand bulkiness. Bulky phosphite ligands usually show much better performance in hydroformylation compared to phosphine ligands due to the combination of steric and electronic effects [39,40].

3.3. Hydroformylation of linalool and β -citronellene in ethanol solutions

The hydroformylation of linalool and β -citronellene was performed also in ethanol, a renewable, low cost and environmentally friendly solvent, to substitute oil industry derivatives such as toluene, commonly used in this reaction. The solvent promoted a significant kinetic effect on the reactions and, under certain conditions, changed the product nature. In general, the reactions with both substrates were ca. two times faster in ethanol than in toluene and showed nearly the same combined selectivity for the hydroformylation products.

Linalool was virtually inactive in ethanol solutions in the absence of phosphorous ligand, similarly to what was found in toluene, probably due to the formation of chelate complexes between linalool and rhodium (Table 5, run 1). The addition of PPh₃ induced the reactivity of linalool toward hydroformylation by cleavage of chelates, with a maximum activity being observed at P/Rh = 10–20 (Table 5, runs 2–6). The reaction gives almost quantitatively the cyclic acetal **1d**, which formally results from the etherification of hemiacetal **1c** with ethanol (Scheme 1). In most

Table 5
Rhodium catalyzed hydroformylation of linalool (**1a**) in ethanol.^a

Run	Ligand	P/Rh	Time (h)	TOF (h ⁻¹)	Selectivity for 1d (%) (<i>cis/trans</i>)
1	None	–	–	<0.5	99 (48/52)
2	PPh ₃	2	12	50	98 (48/52)
3	PPh ₃	5	4	150	97 (73/27)
4	PPh ₃	10	4	190	98 (74/26)
5	PPh ₃	20	4	185	98 (80/20)
6 ^b	PPh ₃	50	4	84	96 (95/5)
7	P(O- <i>o</i> - ^t BuPh) ₃	2	2	200	97 (62/38)
8	P(O- <i>o</i> - ^t BuPh) ₃	5	0.8	520	97 (66/34)
9 ^c	P(O- <i>o</i> - ^t BuPh) ₃	10	0.5	1000	97 (77/23)
10 ^c	P(O- <i>o</i> - ^t BuPh) ₃	20	0.5	1000	97 (85/15)
11 ^c	P(O- <i>o</i> - ^t BuPh) ₃	30	0.5	1000	97 (85/15)

^a Conditions: linalool (0.30 M), [Rh(COD)(OMe)]₂ (0.30 mM), 50 °C, 20 atm (CO/H₂ = 1/1), ethanol. For most of the run the reaction time is given for nearly complete conversions. Conversion and selectivity are based on the substrate reacted. TOF – initial turnover frequency (mol of the substrate converted per mol of Rh per hour).

^b 57% conversion for 4 h.

^c Average TOF is given as the reaction was too fast.

of the runs, small to medium amounts of **1c** were detected in the reaction solutions at incomplete linalool conversions.

The use of P(O-*o*-^tBuPh)₃ instead of PPh₃ remarkably accelerated the hydroformylation of linalool in ethanol solutions (Table 5, runs 7–11). The reactions in the presence of P(O-*o*-^tBuPh)₃ were ca. 5 times faster than in the presence of PPh₃ under the same conditions. Similarly to the Rh/PPh₃ system, the increase in the P(O-*o*-^tBuPh)₃/Rh ratio up to 10 resulted in higher reaction rates. The stereoselectivity of the cyclization step also strongly depended on the concentration of phosphorous ligand: *cis* and *trans* isomers of acetal were formed in comparable amounts at low P/Rh ratios, whereas at high ligand concentrations the *cis* isomer became the major or the almost exclusive reaction product. Similar trends in stereoselectivity of the cyclization step were for both solvents and both ligands used in the present work. The *cis* isomers of cyclic hemiacetal **1c** and its ethyl ether **1d** arise from the less hindered cyclic rhodium complex (proposed as the reaction intermediate) and are preferred products in the solutions with relatively high concentrations of bulky phosphorous ligands. It is important to note that the efficient etherification of hemiacetal **1c** occurs in the ethanol solutions under the hydroformylation conditions in the absence of any additional acid co-catalyst.

The hydroformylation of β-citronellene also readily occurs in ethanol solution giving aldehydes **2b** and **2c** and corresponding acetals **2d** and **2e** in a nearly quantitative combined yield (Table 6, Scheme 2). In the unmodified system, the reaction at 40 °C was very slow showing ca. 50% conversion in 24 h (Table 6, run 1). The introduction of PPh₃ accelerated the reaction, which was completed in 24 h, and promoted a partial acetalization of the aldehydes (Table 6,

runs 3 and 4). However, a really remarkable kinetic effect was promoted by P(O-*o*-^tBuPh)₃: the initial reaction rates at the same P/Rh ratio and under the same conditions were ca. 20 times higher with P(O-*o*-^tBuPh)₃ than with PPh₃ (Table 6, runs 2 and 3 vs. runs 4 and 5). At P/Rh = 5 the aldehydes were obtained in nearly quantitative combined yield, with only small amounts of corresponding acetals being observed at the end of the reaction (Table 6, run 4). A complete substrate conversion occurred in 1 h. The increase in the P(O-*o*-^tBuPh)₃ concentration (runs 5 and 6) and in reaction temperature (runs 7 and 8) enhanced the acetalization activity of the catalyst. At 80 °C, a substantial part of the primarily formed aldehydes **2b** and **2c** was converted into corresponding acetals **2d** and **2e**. The acetalization step was much slower than the hydroformylation as relative amounts of acetals increased with the reaction time. However, we could not find the reaction conditions to convert completely the aldehydes to the acetals. At longer reaction times the content of acetals did not increase suggesting a thermodynamic equilibrium, whereas at higher temperature the combined selectivity for the hydroformylation products became to decrease due to the formation of numerous unidentified compounds. Thus, the hydroformylation of β-citronellene in ethanol solutions can result, depending on the reaction temperature, either almost exclusively in the aldehyde products or in a mixture of aldehydes and acetals with different organoleptic properties.

It has been previously reported that RhCl₃ in the combination with P(OPh)₃ is an efficient catalyst for the hydroformylation–acetalization of alkenes without the addition of acid co-catalysts [41,42]. Intermediate rhodium-chloro-phosphite complexes having Lewis acidity were suggested as active species

Table 6
Hydroformylation of β-citronellene (**2a**) in ethanol.^a

Run	Ligand	P/Rh	T (°C)	Time (h)	TOF (h ⁻¹)	Selectivity (%)			
						Aldehydes		Acetals	
						2b	2c	2d	2e
1 ^b	None		40	24	18	70	25	5	–
2	PPh ₃	5	40	24	32	63	12	24	1
3	PPh ₃	10	40	24	29	62	11	24	2
4	P(O- <i>o</i> - ^t BuPh) ₃	5	40	1.00	540	66	28	6	–
5	P(O- <i>o</i> - ^t BuPh) ₃	10	40	1.25	550	63	27	8	1
6	P(O- <i>o</i> - ^t BuPh) ₃	20	40	1.25	360	61	22	15	2
7 ^c	P(O- <i>o</i> - ^t BuPh) ₃	5	60	0.25	1600	73	23	4	–
				4.00		48	20	24	2
8 ^c	P(O- <i>o</i> - ^t BuPh) ₃	5	80	0.25	1600	39	19	39	3
				1.00		26	15	50	6

^a Conditions: β-citronellene (0.20 M), [Rh(COD)(OMe)]₂ (0.25 mM), 20 atm (CO/H₂ = 1/1), ethanol. Conversion and selectivity are based on the substrate reacted; the reaction time is given for nearly complete conversions. TOF – initial turnover frequency (mol of the converted substrate per mol of Rh per hour).

^b 55% conversion for 24 h.

^c Average TOF is given as the reaction was too fast.

in the conversion of alkene into aldehyde followed by acetalization. We have tested the $\text{RhCl}_3/\text{P}(\text{O}-o\text{-}^i\text{BuPh})_3$ system in the hydroformylation of linalool and β -citronellene in ethanol solutions. Both reactions gave mainly etherification or acetalization products (ethyl ether **1d** from linalool and acetals **2d** and **2e** from β -citronellene); however, substrate conversions occurred much slower than with $\text{Rh}(\text{COD})(\text{OMe})_2$ as the catalyst precursor. Under the same conditions, when a complete conversion of linalool (Table 5, run 7) and β -citronellene (Table 6, run 8) with $\text{Rh}(\text{COD})(\text{OMe})_2$ occurred for 2 and 0.25 h, respectively; the reactions with RhCl_3 required much longer reaction times (22 and 2 h, respectively).

4. Conclusions

The study of the rhodium-catalyzed hydroformylation of linalool and β -citronellene in toluene and ethanol solutions revealed a remarkable effect of the solvent and the nature of the auxiliary phosphorous ligand on the substrate reactivity and product distribution. The reactions occurs approximately two times faster in ethanol than in toluene and up to twenty times faster in the $\text{Rh}/\text{P}(\text{O}-o\text{-}^i\text{BuPh})_3$ system as compared to the system with PPh_3 . Differently from β -citronellene, linalool is very resistant to hydroformylation in the absence of P ligands, probably, due to the binding through both the double-bond and the hydroxyl group to form stable chelates with rhodium. The appropriate choice of the reaction variables allows for the stereochemistry control in tetrahydrofuran derivatives **1c** and **1d**, which are formed nearly quantitatively in toluene and ethanol solutions, respectively. The hydroformylation of β -citronellene in ethanol solutions can result, depending on the reaction temperature, either almost exclusively in aldehyde products or in a mixture of aldehydes and acetals with different organoleptic properties. Several fragrance compounds can be obtained in high yields through a simple one-pot procedure starting from the substrates easily available from natural bio-renewable resources. It is important to point out that the reactions can be performed in ethanol, an environmentally friendly solvent, in the absence of additional acid co-catalysts and, due to the high reactivity of the substrates induced by bulky phosphite ligand, under mild reaction conditions.

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References

- [1] E. Breitmaier, *Terpenes. Flavors, Fragrances, Pharmaca, Pheromones*, Wiley-VCH, Weinheim, 2006.
- [2] A. Behr, L. Johnen, *ChemSusChem* 2 (2009) 1072–1095.
- [3] H. Mimoun, *Chimia* 50 (1996) 620–625.
- [4] K.A.D. Swift, *Top. Catal.* 27 (2004) 143–155.
- [5] M.J. da Silva, J.A. Gonçalves, O.W. Howarth, R.B. Alves, E.V. Gusevskaya, *J. Organomet. Chem.* 689 (2004) 302–308.
- [6] P.A. Robles-Dutenhefner, K.A. da Silva Rocha, E.M.B. Sousa, E.V. Gusevskaya, *J. Catal.* 265 (2009) 72–79.
- [7] V.V. Costa, M.J. Jacinto, L.M. Rossi, R. Landers, E.V. Gusevskaya, *J. Catal.* 282 (2011) 209–214.
- [8] C.G. Vieira, M.C. de Freitas, E.N. dos Santos, E.V. Gusevskaya, *ChemCatChem* 4 (2012) 795–801.
- [9] C.G. Vieira, J.G. da Silva, C.A.A. Penna, E.N. dos Santos, E.V. Gusevskaya, *Appl. Catal. A* 380 (2010) 125–132.
- [10] P.W.N.M. van Leeuwen, C. Claver (Eds.), *Rhodium Catalyzed Hydroformylation*, Kluwer Academic Publisher, Dordrecht, 2000.
- [11] A.J. Chalk, in: W.M. Lawrence, B.D. Mookherjee, B.J. Willis (Eds.), *Flavors and Fragrances: A World Perspective. Proceedings of the 10th International Congress of Essential Oils, Fragrances and Flavors*, Washington, DC, USA, 1986, pp. 867–882.
- [12] Ciprés, Ph. Kalck, D.-C. Park, F. Serein-Spirau, *J. Mol. Catal.* 66 (1991) 399–407.
- [13] I.S. Sirol, Ph. Kalck, *New J. Chem.* 21 (1997) 1129–1137.
- [14] H.J.V. Barros, J.G. da Silva, C.C. Guimarães, E.N. dos Santos, E.V. Gusevskaya, *Organometallics* 27 (2008) 4523–4531.
- [15] K. Soulantica, S. Sirol, S. Koinis, G. Pneumatikakis, Ph. Kalck, *J. Organomet. Chem.* 498 (1995) C10.
- [16] L. Kollár, G. Bódi, *Chirality* 1 (1995) 121–127.
- [17] C.M. Foca, E.N. dos Santos, E.V. Gusevskaya, *J. Mol. Catal. A* 185 (2002) 17–23.
- [18] F. Azzaroni, P. Biscarini, S. Bordoni, G. Longoni, E. Venturini, *J. Organomet. Chem.* 508 (1996) 59–67.
- [19] C.M. Foca, H.J.V. Barros, E.N. dos Santos, E.V. Gusevskaya, J.C. Bayon, *New J. Chem.* 27 (2003) 533–539.
- [20] H.J.V. Barros, E.V. Gusevskaya, E.N. dos Santos, *J. Organomet. Chem.* 671 (2003) 150–157.
- [21] G.A. Korneeva, M.M. Minkovskii, N.A. Novikov, I.S. Istochnikova, M.M. Potarin, E.V. Slivinskii, *RU* 2058309, 1996.
- [22] M. Benaissa, U.J. Jáuregui-Haza, I. Nikov, A.M. Wilhelm, H. Delmas, *Catal. Today* 79–80 (2003) 419–425.
- [23] J.G. da Silva, H.J.V. Barros, E.N. dos Santos, E.V. Gusevskaya, *Appl. Catal. A* 309 (2006) 169–176.
- [24] M.T. Reetz, S.R. Waldvogel, R. Goddard, *Heterocycles* 52 (2000) 935–938.
- [25] H. Siegel, W. Himmele, *Angew. Chem. Int. Ed.* 19 (1980) 178–183.
- [26] V.A. Semikolenov, I.I. Ilyna, I.L. Simakova, *Appl. Catal. A* 211 (2001) 91–107.
- [27] A.M. Trzeciak, E. Wolszczak, J.J. Ziolkowski, *New J. Chem.* 20 (1996) 365–370.
- [28] K. Nozaki, W. Li, T. Horiochi, H. Takaya, *Tetrahedron Lett.* 38 (1997) 4611–4614.
- [29] S. Sirol, Ph. Kalck, *New J. Chem.* 21 (1997) 1129–1137.
- [30] J.T. Sullivan, J. Sadula, B.E. Hanson, R.J. Rosso, *J. Mol. Catal. A* 214 (2004) 213–218.
- [31] A. Stolle, B. Ondruschka, W. Bonrath, T. Netscher, M. Findeisen, M.M. Hoffmann, *Chem. Eur. J.* 14 (2008) 6805–6814.
- [32] A. Stolle, B. Ondruschka, W. Bonrath, *Eur. J. Org. Chem.* (2007) 2310–2317.
- [33] D.S. Melo, S.S. Pereira-Júnior, E.N. dos Santos, *Appl. Catal. A* 411–412 (2012) 70–76.
- [34] K.C.B. Oliveira, A.G. Santos, E.N. dos Santos, *Appl. Catal. A* 445–446 (2012) 204–208.
- [35] M.C. de Freitas, C.G. Vieira, E.N. dos Santos, E.V. Gusevskaya, *ChemCatChem* (2013), <http://dx.doi.org/10.1002/cctc.201200948>.
- [36] R. Uson, L.A. Oro, J.A. Cabeza, *Inorg. Synth.* 23 (1985) 126–127.
- [37] P.W.N.M. van Leeuwen, C.F. Roobeek, *J. Organomet. Chem.* 258 (1983) 343–350.
- [38] A. van Rooy, E.N. Orij, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Organometallics* 14 (1995) 34–43.
- [39] A.A. Dabbawala, H.C. Bajaj, G.V.S. Rao, S.H.R. Abdi, *Appl. Catal. A* 419–420 (2012) 185–193.
- [40] H. Tricas, O. Diebolt, P.W.N.M. van Leeuwen, *J. Catal.* 298 (2013) 198–205.
- [41] B. El Ali, J. Tijani, M. Fettouhi, *J. Mol. Catal. A* 230 (2005) 9–16.
- [42] B. El Ali, J. Tijani, M. Fettouhi, *Appl. Catal. A* 303 (2006) 213–220.