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Selective hydrogenation of myrcene catalyzed by complexes of ruthenium, chromium, iridium and rhodium

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Abstract

The hydrogenation of myrcene catalyzed by Ru, Cr, Ir and Rh complexes leads to the formation of a complex mixture of mono-, di- and trihydrogenated products. Seven major products have been characterized, showing that they arise from the σ-alkyl and/or η^3-allyl intermediates formed by the reaction of metal catalysts with both terminal C=C bonds of myrcene. A good control of chemoselectivity has been achieved through the appropriate choice of the metal and reaction conditions. Monohydrogenated products have been obtained with excellent combined selectivity of 95–98% at a high conversion of myrcene (>80%). Among the catalysts studied, rhodium complexes show the highest activity and selectivity, especially at temperatures lower than 100 °C.

Keywords: Selective hydrogenation; Myrcene; Ru, Cr, Ir and Rh complexes

1. Introduction

Hydrogenation of organic substrates is an important step in the preparation of various fine chemicals [1–7]. Particularly, selective hydrogenation of naturally occurring monoterpenes represents a promising route to produce compounds that could be further functionalized to oxygenated derivatives, which are commercially important in the pharmaceutical, perfume and flavor industries as well as useful synthetic intermediates and chiral building blocks [8–11]. Myrcene is a naturally occurring acyclic polyunsaturated monoterpene which contains three carbon–carbon double bonds, two of them being conjugated. This monoterpene is also easily available by the industrial pyrolysis of β-pinene, one of the major constituents of pine turpentine [11,12]. For several years, we have been interested in catalytic transformations of various natural products, including myrcene [13,14]. It has been found that achieving a high chemo and, especially, regioselectivity is one of the main challenges facing during the metal catalyzed functionalization of this polyolefin. The selective monohydrogenation of myrcene could produce diolefins which could be further functionalized, e.g., via oxidation or hydroformylation, with better selectivity. However, catalytic hydrogenation of myrcene has been little studied hitherto [15–17].

Herein, we report the results of the study on the hydrogenation of myrcene using different catalysts: 10% Pd/C, [$RuCl_2(CO)_2(PPh_3)_2$], [$RhH(CO)(PPh_3)_3$], [$IrCl(CO)(PPh_3)_2$] and [$Cr(CO)_6$] aiming to achieve a high selectivity to monohydrogenated products.

2. Experimental

2.1. Materials

The following compounds were prepared by literature methods [$RuCl_2(CO)_2(PPh_3)_2$] [18], [$RhH(CO)(PPh_3)_3$] [19] and [$IrCl(CO)(PPh_3)_2$] [20]. [$Cr(CO)_6$] was purchased

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from Strem Chemicals. Myrcene (Aldrich) was distilled before use. Solvents were distilled from the appropriate drying agent under nitrogen.

2.2. Catalytic runs and analysis of the products

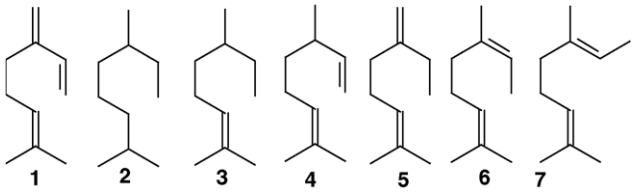
In a typical reaction, a 100 ml 4565 Parr bomb was loaded with catalyst (0.01 mmol), the reaction vessel was closed and three cycles of vacuum-nitrogen were performed. Myrcene (8 mmol) and cyclohexane (50 ml) were loaded under nitrogen through a ball-valved port. The bomb was purged with H_2, pressurized to 20 atm, quickly heated at the desired temperature and continuously stirred at 300 rpm. The pressure was made up to 20 atm with H_2 every once it decreased to 18 atm. Liquid samples were taken when the reaction mixture reached the desired temperature (time zero), at 15 min, at 30 min and then every hour. After 4 h the reactor was cooled to RT, depressurized and opened. The reaction products were identified by GC–MS, ^{1}H and ^{13}C NMR. Routine quantification was performed in a Shimadzu 17A GC instrument fitted with a Carbowax 20M capillary column and a flame ionization detector.

2.3. Spectroscopic studies

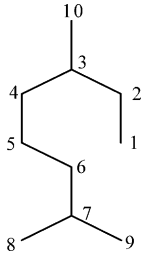
^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Brucker Advance DXR 400 spectrometer (tetramethylsilane, $CDCl_3$). Mass spectra were obtained on a Hewlett-Packard MSD 5890/series II instrument operating at 70 eV.

2.4. Characterization of the products

Based on the analysis of GC–MS, ^{1}H and ^{13}C NMR spectroscopy data of several mixtures of hydrogenated products in different proportions, we proposed the structures of compounds **2**–**7** illustrated in Scheme 1. The assignment of the hydrogen and carbon resonances was carried out by COSY, HMQC (^{1}H, ^{13}C) and DEPT NMR experiments. Spectral simulations performed with the ADC/CNMR program were in agreement with the observed spectra.



Scheme 1.



Spectroscopic data for **2**: MS (*m*/*z*/rel.int.): 142/1 (M^+), 127/1 (M^+–CH_3), 113/10, 85/8, 71/66, 57/100, 56/32. ^{1}H NMR, δ_H (*J*, Hz): 0.85 (br, s, 6H, C^1H_3, $C^{10}H_3$); 0.87 (br, s, 6H, C^8H_3, C^9H_3); 1.12–1.16 (m, 4H, C^2H_2, C^6H_2); 1.23–1.27 (m, 2H, C^5H_2); 1.28–1.35 (m, 3H, C^4H_2, C^3H); 1.47–1.57 (m, 1H, C^7H). ^{13}C NMR, δ_C: 11.45 (C^1), 19.29 (C^{10}), 22.68 (C^9), 22.76 (C^8), 24.90 (C^5), 28.06 (C^7), 29.60 (C^2), 34.52 (C^3), 36.97 (C^4), 39.47 (C^6).

Spectroscopic data for **3**: MS (*m*/*z*/rel.int.): 140/15 (M^+), 111/6, 83/16, 69/100, 55/76. ^{1}H NMR, δ_H (*J*, Hz): 0.85 (br, s, 6H, C^1H_3, $C^{10}H_3$); 1.12–1.16 (m, 2H, C^2H_2); 1.27–1.35 (m, 3H, C^4H_2, C^3H); 1.60 (s, 3H, C^8H_3); 1.67 (m, 3H, C^9H_3); 2.05–2.25 (m, 2H, C^5H_2); 5.08–5.15 (m, 1H, C^6H_2). ^{13}C NMR, δ_C: 11.42 (C^1), 19.92 (C^{10}), 17.60 (C^8), 26.01 (C^9), 31.52 (C^2), 26.60 (C^5), 35.71 (C^4), 34.20 (C^3), 124.40 (C^6), 131.01 (C^7).

Spectroscopic data for **4**: MS (*m*/*z*/rel.int.): 138/4 (M^+), 95/32, 82/44, 67/76, 56/100. ^{1}H NMR, δ_H (*J*, Hz): 0.98 (d, 3H, $C^{10}H_3$, $^3J_{10-3} = 6.7$); 1.25–1.35 (m, 2H, C^4H_2); 1.61 (s, 3H, C^8H_3); 1.67 (m, 3H, C^9H_3); 2.05–2.25 (m, 3H, C^5H_2 C^3H); 5.08–5.15 (m, 1H, C^6H); 4.91 (d, 1H, C^1HH, $^3J_{1-2} = 11.0$); 5.00 (d, 1H, C^1HH, $^3J_{1-2} = 18.0$); 5.69 (ddd, 1H, C^2H, $^3J_{2-1} = 18.0$, $^3J_{2-1} = 11.0$, $^3J_{2-3} = 5.0$). ^{13}C NMR, δ_C: 17.60 (C^8), 20.18 (C^{10}), 25.70 (C^9), 36.84 (C^4), 26.61 (C^5), 37.44 (C^3), 112.50 (C^1), 125.18 (C^6), 131.25 (C^7), 144.77 (C^2).

Spectroscopic data for **5**: MS (*m*/*z*/rel.int.): 138/2 (M^+), 123/4, 109/12, 95/26, 69/100, 53/14. ^{1}H NMR, δ_H (*J*, Hz): 1.03 (t, 3H, C^1H_3, $^3J_{1-2} = 7.4$); 1.61 (s, 3H, C^8H_3); 1.68 (m, 3H, C^9H_3); 2.05–2.25 (m, 6H, C^2H_2, C^4H_2, C^5H_2); 5.08–5.15 (m, 1H, C^6H); 4.71 (br.s, 2H, $C^{10}H_2$). ^{13}C NMR, δ_C: 12.41 (C^1), 17.60 (C^8), 25.70 (C^9), 26.82 (C^5), 28.92 (C^2), 36.33 (C^4), 107.57 (C^{10}), 124.35 (C^6), 131.47 (C^7), 151.43 (C^3).

Spectroscopic data for **6**: MS (*m*/*z*/rel.int.): 138/2 (M^+), 123/4, 95/26, 69/100, 53/12. ^{1}H NMR, δ_H (*J*, Hz): 1.56 (dd, 3H, C^1H_3, $^3J_{1-2} = 6.6$, $^5J_{1-10} = 1.6$); 1.61 (s, 3H, C^8H_3); 1.67 (s, 6H, $C^{10}H_3$, C^9H_3); 2.05–2.20 (m, 4H, C^4H_2, C^5H_2); 5.08–5.15 (m, 1H, C^6H); 5.20 (dq, 1H, C^2H, $^3J_{2-1} = 6.6$, $^4J_{2-10} = 1.4$). ^{13}C NMR, δ_C: 13.22 (C^1), 17.67 (C^8), 23.41 (C^{10}), 25.70 (C^9), 26.41 (C^5), 31.64 (C^4), 119.07 (C^2), 124.50 (C^6), 131.47 (C^7), 135.98 (C^3).

Spectroscopic data for **7**: MS (*m*/*z*/rel.int.): 138/2 (M^+), 123/8, 95/24, 69/100, 53/12. ^{1}H NMR, δ_H (*J*, Hz): 1.59 (br.s, 3H, C^1H_3); 1.61 (s, 3H, C^8H_3); 1.67 (s, 6H, $C^{10}H_3$, C^9H_3); 2.05–2.20 (m, 4H, C^4H_2, C^5H_2); 5.08–5.15 (m, 1H, C^6H); 5.15–5.25 (m, 1H, C^2H). ^{13}C NMR, δ_C: 13.35 (C^1), 17.60

(C^8), 23.41 (C^{10}), 25.70 (C^9), 26.45 (C^5), 39.79 (C^4), 118.29 (C^2), 124.23 (C^6), 131.76 (C^7), 135.80 (C^3).

3. Results and discussion

Hydrogenation of myrcene (**1**) was investigated using Pd, Ru, Cr, Ir and Rh catalysts. Considering the structure of this polyunsaturated substrate, several concurrent transformations may be expected under the catalytic conditions leading to a wide variety of reaction products. We have found that the hydrogenation of myrcene in the presence of a conventional 10% Pd/C catalyst rapidly and exclusively results in the product of a complete hydrogenation, **2** (cyclohexane, 1 wt.% of the catalyst, 80 °C, 20 atm, 30 min). Products of the partial hydrogenation, mono- and diolefins **3**–**7**, can be obtained using Ru, Cr, Ir and Rh complexes, with their combined selectivity and distribution being depended on the catalyst and reaction conditions used.

The results obtained are shown in Table 1. To allow the comparison between the catalysts, the product distribution and combined selectivity for monohydrogenated products are given at about the same extend of conversion of myrcene (ca. 80%).

For all four complexes studied, a rather similar selectivity for monohydrogenated products is observed at 100 °C, with the catalytic activity being strongly dependent on the nature of the metal showing the order of Ru < Cr < Ir < Rh (runs 1–4). Under similar conditions, $[RhH(CO)(PPh_3)_3]$ converts 80% of myrcene within only 5 min, whereas the hydrogenation with $[RuCl_2(CO)_2(PPh_3)_2]$ requires almost 2 h to reach the same conversion (run 4 versus run 1). The selectivity for monohydrogenation slightly differs between ca. 75% when Cr and Ir based catalysts are used to 83–87% for Ru and Rh catalysts.

The distribution of monohydrogenated products is also markedly influenced by the catalyst nature. Although a disubstituted terminal diolefin (**5**) and two stereoisomers of internal diolefin (**6** and **7**) are the major products of the hydrogenation with all four complexes studied, the Ru catalyst promotes a predominant formation of (*E*)-isomer **7** (80% of **6** + **7**, run 1), whereas with the other catalysts (*Z*)-isomer **6** is mainly formed (ca. 70% of **6** + **7**, runs 2–4). Further studies revealed that a good control of the selectivity for monohydrogenated products could be achieved through the addition of extra amounts of phosphorous ancillaries, e.g., PPh_3, or varying the reaction temperature. When the reaction was carried out with $[RhH(CO)(PPh_3)_3]$ and PPh_3 (P/Rh = 20) at 100 °C, the catalytic activity decreased drastically. On the other hand, at 140 °C the reaction in the presence of same amounts of PPh_3 occurs at a reasonable rate showing an excellent combined selectivity of 96% for monohydrogenated products (run 5). A similar effect was observed for the selective hydrogenation of di- and triolefins employing $[RuCl_2(CO)_2(PPh_3)_2]$ as catalyst. The 80% conversion of myrcene is achieved within 4 h (run 5). The hydrogenation of myrcene was also investigated at 80 °C in benzene, with $[RhH(CO)(PPh_3)_3]$ as catalyst. The catalytic activity was still quite high (80% conversion in 1 h), with almost no products of di- and trihydrogenation being formed during this period of time (98% selectivity for monohydrogenation, run 6).

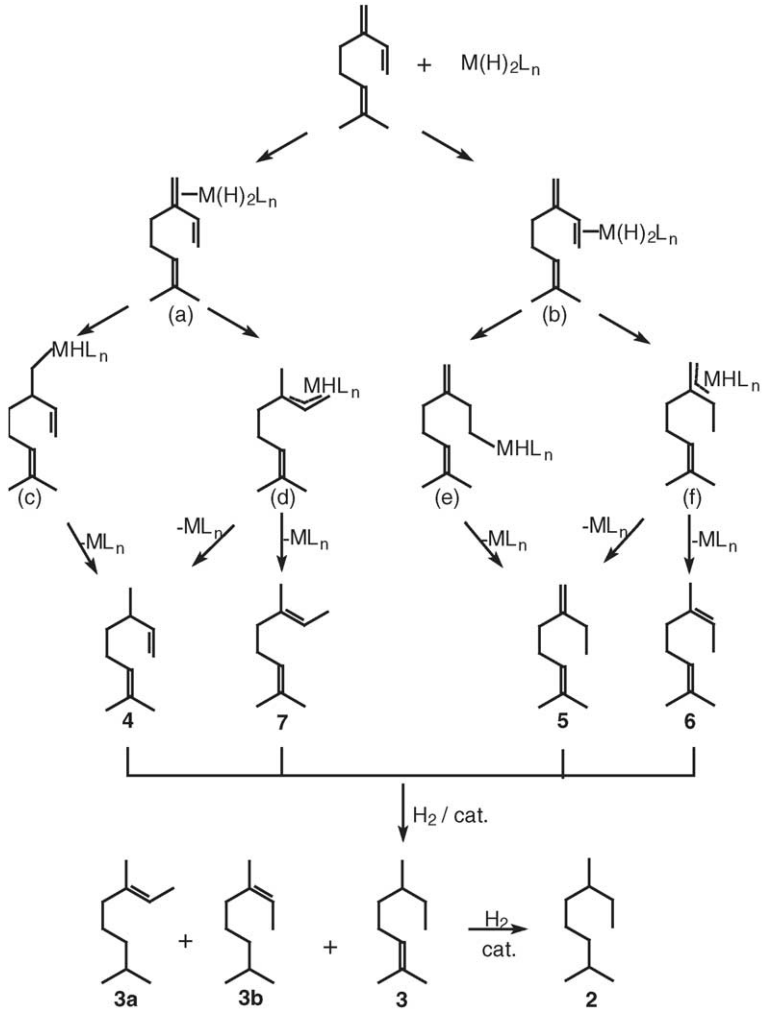
The changes in the product distribution with time are shown in Fig. 1 for the reaction carried out with $[RhH(CO)(PPh_3)_3]$ in cyclohexane at 100 °C. Some information about the concurrent reaction pathways may be extracted from Fig. 1. It can be seen that while myrcene is still present in the reaction medium, the only primary reaction product consumed is monosubstituted terminal olefin **4**. After a complete conversion of myrcene, products **5**–**7** also begin to be further hydrogenated producing **3**, with their reactivity towards hydrogenation decreasing from **5** > **6** > **7**. As the concentration of **3** increases, it reacts further to produce a fully hydrogenated product (**2**). A similar behavior is observed when the reaction is carried out using $[IrCl(CO)(PPh_3)_2]$ (Vaskas's catalyst).

The transformations occurring with myrcene under the hydrogenation conditions can be represented within the framework of a proposed mechanism depicted in Scheme 2. A catalytic cycle of the hydrogenation can involve active metal complexes containing one or two hydride ligands (mono- and dihydride mechanisms, respectively) [21,22]. For the first mechanism, the oxidative addition of the hydrogen to the

Table 1
Hydrogenation of myrcene using different catalysts[a]

Run	Catalyst	Time (min)[b]	*T* (°C)	*S* (%)[c]	Product distribution (%)					
					2	**3**	**4**	**5**	**6**	**7**
1	$[RuCl_2(CO)_2(PPh_3)_2]$	110	100	83	1	16	7	32	9	35
2	$[Cr(CO)_6]$	45	100	74	4	22	8	26	29	11
3	$[IrCl(CO)(PPh_3)_2]$	15	100	76	4	20	8	22	33	13
4	$[RhH(CO)(PPh_3)_3]$	5	100	87	4	9	13	24	34	16
5	$[RhH(CO)(PPh_3)_3]$[d]	240	140	96	tr.	4	14	31	26	25
6	$[RhH(CO)(PPh_3)_3]$[e]	60	80	98	tr.	2	15	27	34	22

[a] *Reaction conditions*: catalyst, 0.01 mmol; myrcene, 8 mmol; solvent (cyclohexane), 50 ml; 20 atm of H_2.
[b] Reaction time necessary for ca. 80% conversion.
[c] Selectivity for monohydrogenated products **4**–**7** at ca. 80% conversion.
[d] PPh_3 was added (0.17 mmol).
[e] Benzene was used as a solvent.



Scheme 2.

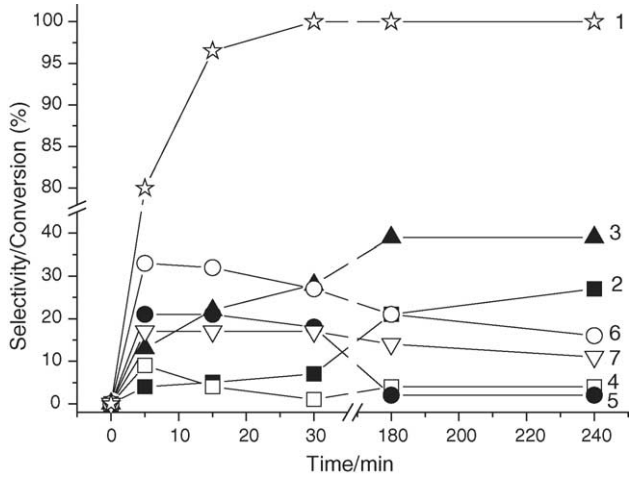


Fig. 1. Hydrogenation of myrcene with [RhH(CO)(PPh_3)$_3$]. *Conditions*: catalyst, 0.01 mmol; myrcene, 8 mmol; solvent (cyclohexane), 50 ml; 20 atm of H_2; 100 °C; for product structures, see Scheme 1.

metal occurs after the insertion of the olefin into a metal-hydride bond, while in the case of the dihydride mechanism the oxidative addition is followed by the insertion. In Scheme 2, the dihydride mechanism is depicted, with the catalyst being represented as $M(H)_2L_n$. Initially, the olefin interacts with a metal center via one of the conjugated double bonds producing intermediates ***a*** and ***b***. Then, the insertion of the olefin into the metal-hydride bond occurs.

If the hydride is transferred to an internal carbon atom, alkyl intermediates ***c*** and ***e*** are formed. These intermediates further evolve to terminal diolefins **4** and **5**, respectively. On the other hand, if the hydride in complexes ***a*** and ***b*** is transferred to a terminal carbon atom, η^3-allyl intermediates ***d*** and ***f*** are formed. The addition of the hydride to a η^3-allylic terminal carbon atom in intermediate ***d*** results in the formation of product **7**, while the transference of the hydride to a η^3-allylic disubstituted carbon atom gives product **4**. The transformation of intermediate ***f*** via a similar reductive elimination leads either to product **5** or **6** depending on the direction of the hydride addition to allylic carbon atoms.

A preferential formation of monohydrogenated products **5** and **6** compared to **4** and **7** has been observed in most of the systems studied (Table 1; Fig. 1). This result is expected from the analysis of Scheme 2, since the first two products arise from the intermediates formed through the reaction of the metal catalyst with the less substituted C=C bond of myrcene.

Primarily formed diolefins **4**–**7** can undergo further hydrogenation to produce **3**, which, in its turn, can be hydrogenated giving the fully saturated product **2**. In addition, small amounts of some unidentified products have been detected in the reaction solutions, which can be attributed to monolefins **3a** and **3b** or other products of the possible isomerization of olefins **3**–**7** catalyzed by the same metal complexes operating in hydrogenation.

It should be mentioned that the product distribution for myrcene hydrogenation depends not only on which reaction pathway is the most favorable kinetically under certain conditions but also on the competition between the olefins for coordination sites on the metal. Therefore, the reactivity of a particular olefin depends not only on its nature and its concentration but also on the nature and concentration of the other olefins present in the reaction medium. This makes the balance between the reaction pathways very complicated. It is reasonable to suggest that pathways involving η^3-allyl intermediates are kinetically favorable and that conjugated olefins are preferably coordinated to the metal center via the formation of η^4-diolefin complexes. Thus, it can be expected that while myrcene is still present in the reaction solutions in appreciable amounts, no further hydrogenation of primarily formed diolefins **4**–**7** occurs to a considerable extent. However, after the complete conversion of myrcene, the rate of the hydrogenation of the non-conjugated olefins increases. The following reactivity towards hydrogenation is expected [23]: monosubstituted terminal olefin **4** > 2-2′-disubstituted terminal olefin **5** > (*Z*)-isomer of trisubstituted olefin **6** > (*E*)-isomer of trisubstituted olefin **7**. The reactivities of internal diolefins **6** and **7** are similar to that of olefin **3**, which contains only one trisubstituted double bond. Thus, the hydrogenation of **6** and **7** is accompanied by the hydrogenation of **3** resulting in the saturated product **2**.

4. Conclusion

The hydrogenation of myrcene catalyzed by Ru, Cr, Ir and Rh complexes leads to the formation of a complex mixture of mono-, di- and trihydrogenated products. We have achieved a good control of chemoselectivity through the appropriate choice of the metal and reaction conditions. Monohydrogenated products can be obtained with excellent combined selectivity of 95–98% at a high conversion of myrcene (>80%). Among the catalysts studied, rhodium complexes show the highest activity and selectivity, especially at temperatures below 100 °C. The selective monohydrogenation of myrcene could be a useful method to produce a mixture of diolefins of different reactivity, which could be further transformed to oxygenated derivatives with selectivities better than myrcene itself. Studies on the metal complex catalyzed oxifunctionalization of these mixtures are in progress in our laboratory.

Acknowledgements

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