

SELECTIVE HOMOGENEOUS HYDROGENATION OF CONJUGATED DIOLEFINS TO MONOOLEFINS CATALYZED BY SOME RHODIUM PHOSPHINE COMPLEXES

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(Received September 17th, 1973)

Summary

Selective hydrogenation of 1,3-diolefins to mainly terminal monoolefins was carried out in the presence of $\text{RhH}(\text{PPh}_3)_4$ and $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$ as homogeneous catalysts. Under identical conditions cycloolefins were slowly obtained from cycloolefins.

Introduction

Homogeneous hydrogenation by means of rhodium complexes has been extensively investigated [1–5]. As already reported, the selective hydrogenation of carbon–carbon double bonds in molecules containing other potentially reducible groups can be achieved using catalysts such as $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [6, 7]. The former catalyst was also reported to effect the selective hydrogenation of conjugated 1,3-diolefins, yielding mainly internal olefins. For instance, hydrogenation of 1,3-pentadiene catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ occurred with initial attack at the terminal unsaturation and consequent formation of 2-pentene [8]. In the course of our investigations, we had observed that $\text{RhH}(\text{PPh}_3)_4$ [9, 11] and $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$ [11] catalyzed the stereo-selective hydrogenation of 1,3-dienes to α -olefins [12], one of only a few examples of homogeneously catalyzed hydrogenations of 1,3-dienes to terminal monoenes that has been described*.

*The hydrogenation of isoprene and 2,3-dimethyl-1,3-butadiene using $\text{RhCl}(\text{PPh}_3)_3$ with formation of terminal monoolefins as the main products has been recently reported [13].

Results

It is known that triphenylphosphine complexes do not easily dissolve; that is the reason why we prepared our catalytic systems by adding some triethylphosphine to a suspension of $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$ (I) and $\text{RhH}(\text{PPh}_3)_4$ (II) at a PEt_3 to Rh ratio of 1/1. In this way the rhodium complexes dissolved quite easily with formation of a homogeneous solution. Hydrogenation was carried out under a constant hydrogen pressure of 15 atm. and at $50\text{--}120^\circ$. In order to obtain selective hydrogenation the reaction mixture was quenched when the hydrogen adsorption rate, which was fairly constant for the whole reaction, showed a substantial increase corresponding to the subsequent hydrogenation of the resulting monoenes. Under these conditions (for more details, see experimental) in the hydrogenation of 1,3-dienes, selectivities to monomers as high as 80 - 95% were obtained. No solvent effect on either catalyst activity or selectivity was observed; all runs described here were carried out using either cyclohexane or dioxane as solvents.

Figure 1 shows the results for hydrogenation of butadiene catalyzed by $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$. A constant selectivity (over 90%) to intermediate monoenes was observed up to a certain diene conversion, then it sharply decreased with the formation of butane. There is a substantial stereoselectivity, with over 80% of the total monoenes being 1-butene.

The introduction of a methyl group into the 1,3 conjugated system decreases both the selective formation of monoolefins (see Table 1 and Figs. 2 and 3) and the stereoselective formation of α -olefins. Although kinetic data are not yet available it is clear (Table 1) that $\text{RhH}(\text{PPh}_3)_4$ is more active and selective than $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$, the latter requiring more drastic reaction conditions. Moreover, in the case of $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$ an induction period was always observed, which probably indicates that a transformation of the initial rhodium complex into a catalytically active species was necessary. Although such a linear internal diolefin as 2,4-hexadiene could not be hydrogenated at all under conditions similar to those reported above, we achieved hydrogenation of conjugated (cyclopentadiene, 1,3-cyclooctadiene) and unconjugated (1,5-cyclooctadiene) cyclic diolefins to monoolefins with high selectivity (Table 2). With these compounds more drastic reaction conditions had to be used in order to ob-

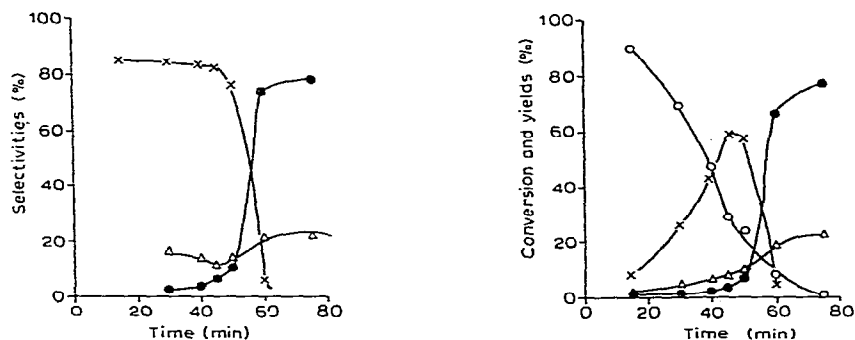


Fig. 1. Hydrogenation of butadiene with $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6 + 2\text{PEt}_3$. Dioxane: 8.3 ml; Catalyst: 0.21×10^{-3} mol; substrate: \circ Butadiene; \times 1-butene; \triangle 2-butenes; \bullet butane.

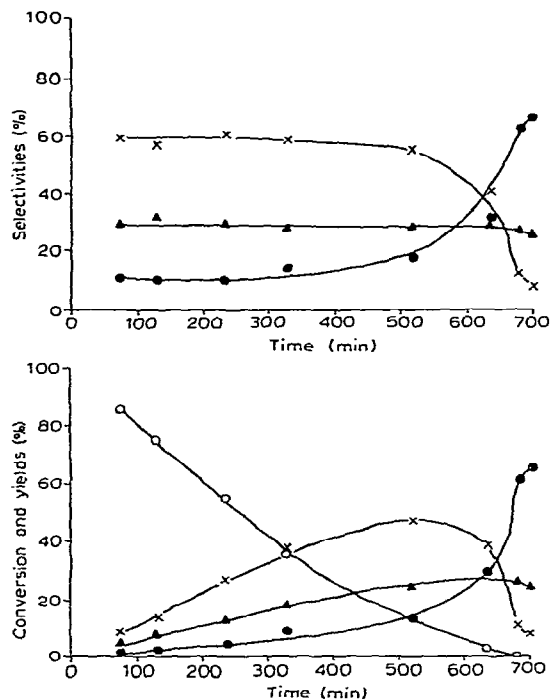


Fig. 2. Hydrogenation of 1,3-pentadiene with $\text{RhH}(\text{PPh}_3)_4 + \text{PEt}_3$. Cyclohexane: 16.5 ml; catalyst: 0.21×10^{-3} mol; substrate: 14×10^{-2} mol; hydrogen pressure: 15 atm; temp.: 46°C . \circ 1,3-Pentadiene; \times 1-pentene; \blacktriangle 2-pentenes; \bullet pentane.

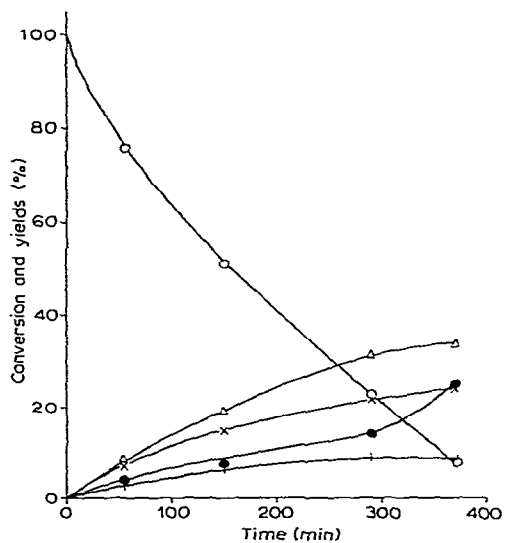


Fig. 3. Hydrogenation of isoprene with $\text{RhH}(\text{PPh}_3)_4 + \text{PEt}_3$. Cyclohexane: 8.3 ml; catalyst: 0.21×10^{-3} mol; substrate: 7×10^{-2} mol; hydrogen pressure: 15 atm; temp.: 92°C . \circ Isoprene; \times 2-methyl-1-butene; \blacktriangle 2-methyl-2-butene; \bullet 2-methyl-butane.

TABLE 1
SELECTIVE HYDROGENATION OF CONJUGATED DIENES

Substrate 7×10^{-2} mol; solvent 8.3 ml; catalyst: as Rh 0.21×10^{-3} mol; hydrogen pressure 15 atm. I is $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$; (II) is $\text{RhH}(\text{PPh}_3)_4$. 1,3-Pentadiene is 81% *trans* and 19% *cis*.

Substrate (% convn.)	Catalyst and solvent	Temp. (°C)	Time (min.)	Products (%)
1,3-Butadiene (69)	I + 2PEt ₃ dioxane	65	45	1-Butene (82.7) <i>cis</i> -2-Butene (4.7) <i>trans</i> -2-Butene (6.8) Butane (5.8)
1,3-Butadiene (60)	I + 2PEt ₃ cyclohexane	65	45	1-Butene (82.5) <i>cis</i> -2-Butene (4.8) <i>trans</i> -2-Butene (6.8) Butane (5.9)
1,3-Pentadiene (48)	I + 2PEt ₃ dioxane	65	45	1-Pentene (59.0) <i>cis</i> -2-Pentene (9.8) <i>trans</i> -2-Pentene (12.6) Pentane (18.6)
1,3-Butadiene (65)	II ^a + PEt ₃ cyclohexane	50	100	1-Butene (87.0) <i>cis</i> -2-Butene (3.8) <i>trans</i> -2-Butene (5.7) Butane (3.5)
1,3-Pentadiene (64) ^b	II + PEt ₃ cyclohexane	46	330	1-Pentene (60.0) <i>cis</i> -2-Pentene (15.0) <i>trans</i> -2-Pentene (14.0) Pentane (11.0)
Isoprene (68)	I + 2PEt ₃ cyclohexane	92	330	2-Methyl-1-Butene (21.2) 2-Methyl-2-Butene (42.0) 3-Methyl-1-Butene (4.8) 2-Methyl-Butane (32.0)
Isoprene (79)	II + PEt ₃ cyclohexane	92	290	2-Methyl-1-Butene (29.0) 2-Methyl-2-Butene (41.0) 3-Methyl-1-Butene (13.0) 2-Methyl-Butane (17.0)
2,4-Hexadiene (0)	I + 2PEt ₃ cyclohexane	120		no reaction

^a The catalyst was 0.1×10^{-3} mol. ^b Substrate and solvent were respectively 14×10^{-2} mol and 16.5 ml.

tain acceptable hydrogenation rates compared with the earlier compounds. With 1,5-cyclooctadiene, isomerization to 1,3-cyclooctadiene occurred before hydrogenation. In the cyclopentadiene hydrogenation, the diolefin dimerization occurred more rapidly than selective hydrogenation. However, if the dimer is considered as an unconverted product, the selectivity to cyclopentene is as high as 91%.

TABLE 2
SELECTIVE HYDROGENATION OF CYCLODIENES

Substrate 7×10^{-2} mol; solvent 6.4 ml.; $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6 + 2\text{PEt}_3$ is the catalyst (0.21×10^{-3} mol); hydrogen pressure 15 atm.

Substrate (% convn.)	Catalyst and solvent	Temp. (°C)	Time (h)	Products (%)
1,5-Cyclooctadiene (98.7)	Cyclohexane	90	16	1,3-Cyclooctadiene (39.2) Cyclooctene (59.0) Cyclooctane (1.8)
1,3-Cyclooctadiene (38)	Cyclohexane	100	10	Cyclooctene (99.7) Cyclooctane (0.3)
Cyclopentadiene (90)	Dioxane	95	4	Cyclopentene (14.3) Cyclopentane (1.3) Dicyclopentadiene (84.4)

Discussion

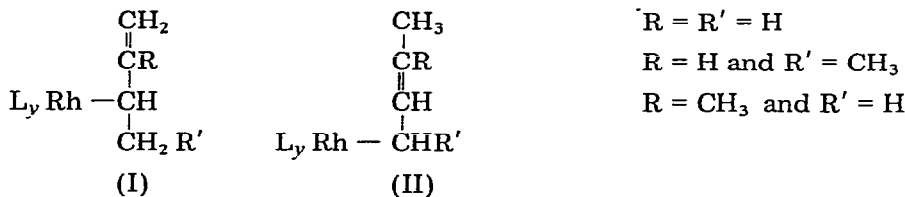
Selective hydrogenation of 1,3-dienes has been recently reviewed [6,7]. Usually, high selectivity is achieved with complexes which do not hydrogenate monoolefins, such as $\text{Co}(\text{CN})_5^{3-}$, or which very slowly hydrogenate the internal monoolefins formed, such as $\text{RhCl}(\text{PPh}_3)_3$ or $\text{RuHCl}(\text{PPh}_3)_3$. In both cases the selectivity is kinetically controlled [6]. In the work reported here we observed a high selectivity toward formation of α -monoenes, which however, could be easily hydrogenated by the same catalytic systems, as is found in the selective heterogeneous hydrogenation of dienes. Such selectivity is maintained until a specific residual concentration of the diene is reached. Therefore, this is a thermodynamically controlled selectivity due to the strong interaction of residual diolefin with the catalytic system. A similar behaviour, but with a lower selectivity, was described for hydrogenations catalyzed by $[\text{Co}(\text{CO})_2\{\text{P}(\text{n-but})_3\}]_3$ and $\pi\text{-C}_4\text{H}_7\text{Co}(\text{CO})_2\{\text{P}(\text{n-but})_3\}$ [14]. In both cases, the strength of the diene-metal interaction probably is the most important factor for selectivity control. The different values of the observed selectivities could reflect the tendency of 1,3-dienes to form allyl intermediates that are more stable for rhodium than for cobalt, which is not unexpected.

Stereoselectivity in the reaction merits some discussion. Usually, for many catalytic systems, the assumption has been made that σ -alkenyl and/or π -allyl species are involved as intermediates [6]. Evidence exists concerning the formation of these complexes by diene insertion into metal-hydrogen bonds. σ -Alkenyl and π -allyl structures have been detected in the pentacyanocobaltate-catalyzed hydrogenation of dienes and the existence of a σ - π equilibrium has been proposed to explain the distribution of the hydrogenation products and stereoselectivity.

Similar intermediates could probably also be postulated for rhodium complexes. When σ -alkenyl and π -allyl species are involved, formation of terminal or internal olefins can be related to their structure: σ -alkenyl species should give either a terminal or an internal olefin, whilst π -allyl species should give only a mixture of both olefins. In our case σ -alkenyl species should predominate because of the presence of an excess of ligand which affects the σ - π conversion (eqn. 1).



On the basis of the experimental results we can postulate that σ -alkenyl structures like I or II could be present, with I being predominant for butadiene and 1,3-pentadiene. Methyl substitution in isoprene could exert considerable steric and electronic effects, which would affect the equilibrium (1) and the σ -alkenyl structures; II could be predominant in this case.



As regards the formation of α -olefin we can add that it reflects the composition of the direct hydrogenation products and is due to the very poor isomerization properties of the catalytic systems here employed. In fact, we observe not only the predominant presence of α -olefins, but also that the *cis-trans* ratio of 2-olefins is very far from the equilibrium value and is fairly constant during the reaction period (Figs. 1 and 2).

Experimental

The zero-valent complex $[\text{Rh}(\text{CO})_2\text{PPh}_3]_2 \cdot 2\text{C}_6\text{H}_6$ or the hydride complex $\text{RhH}(\text{PPh}_3)_4$ prepared as previously reported [11] were dissolved before use. Yellow solutions "in vitro" were obtained either in dioxane or in cyclohexane by adding a small amount of triethylphosphine ($\text{PEt}_3/\text{Rh} = 1$) and bubbling hydrogen slowly through the solution. In a typical experiment, the catalytic solution was introduced into a 50 ml stainless steel autoclave previously purged with an inert gas; it was then charged with diolefin and hydrogen was pumped in. The temperature was reached by heating the batch quickly. Pressure was kept constant for the duration of the reaction by replenishing the gas as it was consumed. As a rule with 1,3-diolefins, the batch was rapidly quenched when the rate, nearly constant for most of the reaction, showed a substantial increase. The product, on cooling, was a light yellow solution when using 1,3-diolefins, but was dark red when using cycloolefins.

Analyses were carried out by gas-chromatography either on the final product or on a small sample drawn from the autoclave during the reaction.

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