Highly selective hydroformylation of internal and terminal olefins to terminal aldehydes using a rhodium-BIPHEPHOS-catalyst system

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Abstract

In this paper, we describe the hydroformylation of terminal and internal olefins to terminal aldehydes using a catalyst system of rhodium and BIPHEPHOS. According to industrial processes, the catalyst concentration lies in a range from 0.01 to 0.001 mol%. The conversions are, depending of the substrate, up to 99% and yields up to 86% of the aldehydes can be found. The ratio of linear to branched products is up to 99:1.
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1. Introduction

The hydroformylation of olefins, also known as oxo-process, is one of the most important processes using transition metal catalysis in industry [1,2]. More than eight million tons per year of several aldehydes are produced in this way.

The reaction is carried out in a homogenous system using a cobalt- or rhodium-based catalyst-system. The advantages when using rhodium instead of cobalt are lower temperatures and pressures of syngas, higher conversions, yields and selectivities [3].

Apart from the selection of the metal the choice of the ligand plays a very important role in hydroformylation. Some ligands seem to allow a hydroformylation without any isomerization [4], other ligands isomerize internal olefins first and hydroformylate to yield only the terminal aldehyde [5]. In addition to isomerization, the hydrogenation is an important side-reaction (Scheme 1).

For hydroformylation reactions, phosphorous ligands are mainly used. Beller and colleagues hydroformylated with rhodium-phosphite-catalyst-system 2-pentene with a selectivity of 90% to *n*-hexanal [6]. BIPHEPHOS **1**, a phosphite-ligand, was sythesized by Billig et al. at UCC (Union Carbide Cooperation) [7,8]. *trans*-4-Octene was hydroformylated with rhodium as metal with high regioselectivity to *n*-nonanal by Behr et al. [9]. Börner et al. showed that BIPHEPHOS together with other phosphite ligands leads to very high selectivites and linear:branched ratios, too [10].

The kinetics of isomeriszation of linear olefins and of the isomerization followed by hydroformylation was examined by Behr et al. with *trans*-4-octene and 1-octene as model compounds Fig. 1 [11].

In our experiments, we used several terminal olefins, one internal and one functionalized olefin (Scheme 2).
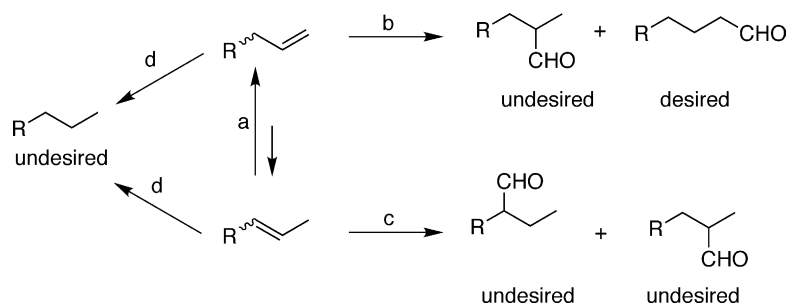
2. Experimental

2.1. Reagents

All olefins were purchased from Fluka or Sigma–Aldrich and used without purification. The solvent (toluene abs., dried) was purchased from Fluka. The catalyst precur-

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Scheme 1. Selective hydroformylation of olefins to linear aldehydes: (a) isomerization, (b) hydroformylation of a terminal olefin, (c) hydroformylation of internal olefins and (d) hydrogenation of terminal and internal olefins.
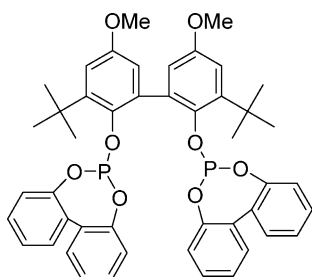

Fig. 1. BIPHEPHOS **1**.

sor Rh(CO)$_2$acac was received from Strem, the syngas (CO:H$_2$ = 1:1) from Linde. The chelating ligand BIPHEPHOS **1** was synthesized according to the work of Cuny and Buchwald [12].

2.2. General procedure of hydroformylation experiments

All hydroformylation experiments were carried out simultaneous in two 100 ml laboratory reactors from Parr Instrument Company, Moline, IL, USA. The reactants were filled into the vessel and then the reactor was secured and flushed three times with argon. After flushing three times with syngas, a syngas pressure of 30 bar was adjusted.

In a typical hydroformylation experiment, 1 ml of a solution of 4.5 µmol Rh(CO)$_2$acac in toluene abs., 22.5 µmol

Scheme 2. Used olefins: 1-pentene **2**, 1-hexene **3**, 1-octene **4**, 1-decene **5**, 1-dodecene **6**, *trans*-2-pentene **7a** and *cis*-2-pentene **7b**, hex-5-en-1-ol **8**.

(18 mg) BIPHEPHOS (Rh:ligand = 1:5) and 45 mmol olefin were dissolved in 15 ml abs. toluene. The vessel was closed and prepared as described above. The stirrer was adjusted to 1000 rpm. The autoclave was heated to the desired temperature within 30 min. After the reaction time, the vessel was cooled down to room temperature within a few minutes by cooling with an ice bath, depressurized, flushed with argon and opened to obtain a sample for a GC- and GC/MS-analysis. GC-experiments were performed on an HP 5 column (30 m) with an FID-detector, temperature profile: 50 °C, 8 K/min—260 °C, 5 min const.; 8 K/min—280 °C, 5 min const.; 8 K/min—300 °C, const.

3. Results and discussion

The used catalyst system showed very high activities and regioselectivities between 80 and 180 °C. With regard to the regioselectivity, the best results were obtained in the region from 80 to 120 °C. Van Leeuwen and colleagues presented a catalytic system which is able to hydroformylate 1-octene to *n*-nonanal with a selectivity of up to 68:1 and a TOF of 1100 h^{-1} [13]. We were able to get a regioselectivity of 98:2 for the *n*-nonanal and a TOF of 7800 h^{-1}. For the hydroformylation of 1-pentene, we obtained 9% aldehydes after 4 h and 37% after 48 h at 80 °C with a linear:branched ratio of 99:1. At 100 °C, an aldehyde yield of 86% was reached after 16 h at an overall conversion of 91%. Under these conditions, the ratio linear:branched is 99:1 as well. The activity is lower at these temperatures, but the selectivity is excellent, too. At high temperatures (120 °C or higher), after a reaction time of 1 h conversion from ≥88% up to 99% were obtained. Observed yields are in the range of 70 to 82%. The byproducts of the reaction, alkanes and isomeric olefins, are obtained as byproducts from hydrogenation and isomerization, respectively (Table 1).

To investigate the potential of this catalyst system, we carried out reactions with a rhodium-substrate-ratio of 1:100,000. We achieved a very high TOF of 44,000 h^{-1} after a reaction time of 1 h. All TOFs were calculated for the reaction time, although a small part of the reaction takes place during the heating time. We consider these initial conversions as neglectable due to the lower reaction rate at lower tempera-
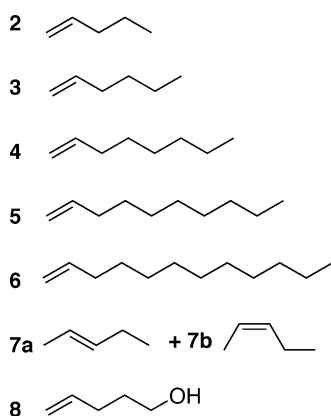
Table 1
Hydroformylation of 1-alkenes (Rh:olefin = 1:10,000, reaction time: 60 min, p_{CO/H_2} = 30 bar)

Substrate	T (°C)	Conversion[a] (%)	Aldehyde[a] (%)	Alkane[a] (%)	iso-Alkenes[a] (%)	TOF (h^{-1})	*l:b* ratio
1-Pentene **2**[b]	160	97	76	20	1	1,895	>99:1
1-Hexene **3**	120	88	82	1	5	8,200	>99:1
1-Octene **4**	120	99	78	1	20	7,800	98:2
1-Decene **5**	120	90	78	2	10	7,800	99:1
1-Dodecene **6**	120	91	70	2	19	7,000	97:3
1-Dodecene **6**[c]	140	70	44	1	25	44,000	99:1
Hex-5-en-1-ol **8**	120	95	75	1[d]	19	7,500	>99:1

[a] Determined by GC/GC–MS.
[b] t = 240 min.
[c] Rh:olefin = 1:100,000.
[d] Alcohol.

Table 2
Hydroformylation of 1-dodecene (Rh:olefin = 1:10,000, reaction time: 60 min, p_{CO/H_2} = 30 bar)

| T (°C)	Conversion (%)	Aldehydes (%)	iso-Alkenes (%)	TON	TOF (h^{-1})	*l:b* ratio
160	99	61	38	9900	6100	97:3
140	99	70	29	9900	7000	98:2
120	99	61	38	9900	6100	97:3
100[a]	98	73	25	9800	1460	98:2
80[b]	97	73	25	9700	730	99:1

[a] t = 5 h.
[b] t = 10 h.

tures [14]. The heating rate of a Parr autoclave is not linear, so we cannot give an exact time for different temperatures. We know, that below 100 °C the catalyst works slowly (Table 2).

1-Dodecene was hydroformylated at 140 °C and a syngas pressure of 30 bar. The conversion was 70%, the yield of tridecanal was 44% and the yield of dodecane was 25%. The linear:branched ratio was 99:1. These results point out the very high activities and regioselectivities that can be achieved with this catalyst system.

The used catalytic system isomerizes the terminal olefins to internal olefins as most of the known systems. But the very high regioselectivity we got shows the advantage of BIPHEPHOS. In the hydroformylation reaction, exclusively the terminal olefins were converted out of the mixture of terminal and internal olefins present in the reaction mixture (Table 1). The problems of isomerization of terminal olefins and the catalytic cycle were described in [14–17].

Table 2 demonstrates the differencies in the activity of the BIPHEPHOS-rhodium-complex and the very high regioselectivity of the hydroformylation of 1-dodecene at different temperatures. The activity of this system increases with higher temperatures. The regioselectivity decreases slowly. The best results for the production of aldehydes were found at 140 °C. The TON and the TOF are also very high at this temperature.

The BIPHEPHOS-rhodium system seems to hydroformylate only terminal alkenes. The reactions rates of the used system are lower than those of other catalytic systems. The hydroformylation of internal alkenes is sterically hindered by the ligand, so we get a very high linear:branched ratio. The isomerization is the most important byreaction and we are
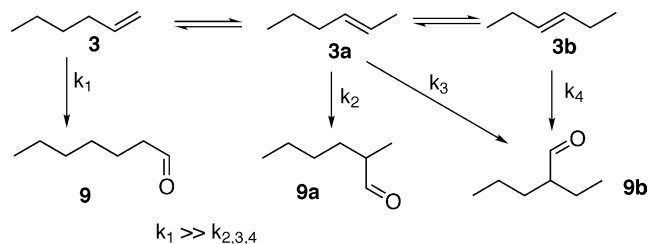
Scheme 3. Isomerization of 1-hexene **3** to 2-hexene **3a** and 3-hexene **3b** and hydroformylation to the corresponding aldehydes **9**, **9a** and **9b**.

not able to suppress it. The best results for a high aldehyde yield and a low isomerization rate is given for a reaction time of 60 min at our conditions as described in Section 2.

Scheme 3 illustrates the reaction for 1-hexene **3**. The isomerization is a reaction with a quite high velocity. This is very well shown by Behr et al. [11]. So, 1-hexene **3** isomerizes to 2-hexene **3a** and 3-hexene **3b** until a equilibration state is reached. The reaction rate for the hydroformylation of the terminal hexene **3** is much higher than the reaction rates for the hydroformylation of the internal hexenes **3a** and **3b**. The amount of 1-hexene **3** decreases and because of equilibration of the isomerization there is a "back-isomerization" of **3a** to **3** and also of **3b** to **3a**. These are the reasons of the very high regioselectivity and the high isomerization rates of this catalytic system.

The conversion of the functionalized alkene hex-5-ene-1-ol **8**, also shows very good activity and regioselectivity (Scheme 4).

At 130 °C, a reaction time of 1 hour and a syngas pressure of 30 bar a conversion of 95% was reached. 20% of the olefin
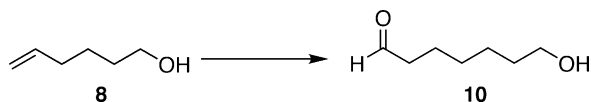
Table 3
Hydroformylation of 2-pentene **7a** and **7b**, reaction time: 60 min, Rh:olefin = 1:10,000.

	Conversion[a] (%)	Aldehyde[a] (%)	Alkane[a] (%)	TOF (h^{-1})	*l:b* ratio
1[b]	99	79	20	1975	>99:1
2[c]	91	86	5	538	>99:1

[a] Determinated by GC–MS.
[b] $T = 160\,^\circ$C, $t = 4$ h.
[c] $T = 100\,^\circ$C, $t = 16$ h.

Scheme 4. Hydroformylation of hex-5-ene-1-ol **8** to 7-hydroxyheptanal **10**.
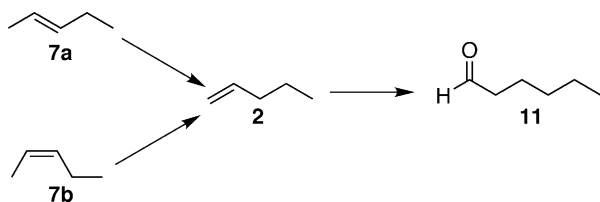
Scheme 5. Isomerization of **7a** and **7b** to **2** and following hydroformylation to **11**.

8 was hydrogenated to hexanol, 75% was converted to 7-hydroxyheptanal **10** with a linear:branched ratio of more than 99:1. The GC analysis showed no other isomers than the *n*-isomer of product **10**.

The reaction of a mixture of *trans*-2-pentene **7a** and *cis*-2-pentene under the same conditions shows that there is no hydroformylation at the secondary carbon, rather an isomerization takes place (Scheme 5). The only aldehyde present is 1-hexanal **11**, so the linear:branched ratio is 99:1.

30% yield of aldehydes were achieved at 80 °C after 24 h also with high linear:branched ratio of 99:1. At this temperature the activity of the catalyst is lower, but the regioselectivity is excellent, too. Beller and colleagues used 2-pentene in a combined isomerization–hydroformylation reaction. With their ligand they got yields from 21 to 68% and regioselectivities to the *n*-hexanal from 89:11 up to 95:5. Their TOFs were about 69 up to 425 h^{-1} [6]. We were able to achieve a regioselectivity of more than 99:1 by yields up to 86% and TOFs up to 1975 h^{-1}. Compared to these known results, our catalytic system shows higher yields, regioselectivites and TOFs (Table 3).

4. Conclusions

We showed that the known catalyst system of rhodium and BIPHEPHOS is able to hydroformylate several terminal alkenes with high yields (up to 82%) and high activities (TOF is up to 8200 h^{-1}) to aldehydes with a high ratio of linear:branched of 97:3 up to more than 99:1. We also showed that this system is able to work in a very high substrate-rhodium-ratio of 100,000:1. There we found a high TOF of 44,000 h^{-1} after a reaction time of 1 h. Such activity was not reported before for a hydroformylation together with this high regioselectivities. Performing this reaction under the described conditions it is also possible to reach linear:branched ratio up to 99:1.

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