

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 synthesized 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 selectivities and linear:branched ratios, too [10].

The kinetics of isomerization 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).

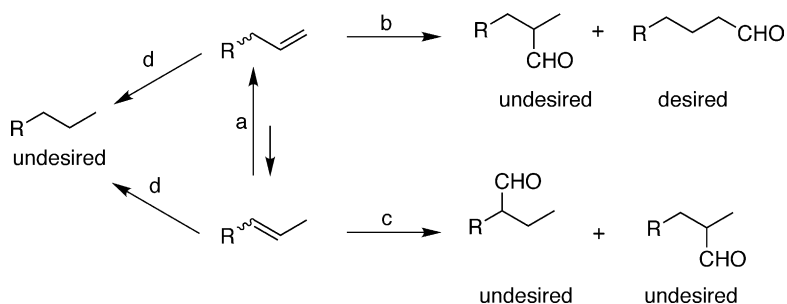
2. Experimental

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 precursor

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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.

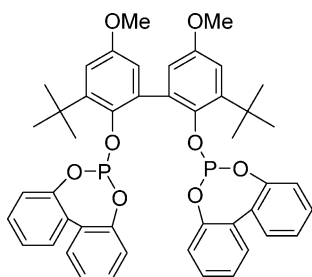


Fig. 1. BIPHEPHOS 1.

sor $\text{Rh}(\text{CO})_2\text{acac}$ was received from Strem, the syngas ($\text{CO}:\text{H}_2 = 1:1$) 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 simultaneously 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.

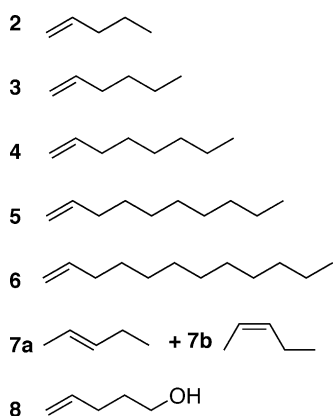
In a typical hydroformylation experiment, 1 ml of a solution of 4.5 μmol $\text{Rh}(\text{CO})_2\text{acac}$ in toluene abs., 22.5 μmol

(18 mg) BIPHEPHOS ($\text{Rh}:\text{ligand} = 1:5$) 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 $^\circ\text{C}$, 8 K/min—260 $^\circ\text{C}$, 5 min const.; 8 K/min—280 $^\circ\text{C}$, 5 min const.; 8 K/min—300 $^\circ\text{C}$, const.

3. Results and discussion

The used catalyst system showed very high activities and regioselectivities between 80 and 180 $^\circ\text{C}$. With regard to the regioselectivity, the best results were obtained in the region from 80 to 120 $^\circ\text{C}$. 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 $^\circ\text{C}$ with a linear:branched ratio of 99:1. At 100 $^\circ\text{C}$, 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 $^\circ\text{C}$ or higher), after a reaction time of 1 h conversion from $\geq 88\%$ 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-



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**.

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