



# Highly selective tandem isomerization–hydroformylation reaction of *trans*-4-octene to *n*-nonanal with rhodium-BIPHEPHOS catalysis

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This contribution is dedicated to our fellow Sascha Glatzel who left too early

## Abstract

This paper describes the synthesis of *n*-nonanal by a consecutive isomerization–hydroformylation reaction of *trans*-4-octene using a homogeneous catalyst system consisting of Rh(acac)(CO)<sub>2</sub> and BIPHEPHOS. In the presence of syngas these two precursor molecules form in situ the catalytically active species. At a reaction temperature of 125 °C and a syngas pressure of 20 bar the linear C<sub>9</sub>-aldehyde is formed in the solvent toluene in 88% yield and only few amounts of the saturated hydrocarbon and the branched C<sub>9</sub>-aldehydes are obtained. In comparison to industrial applications the catalyst concentration has quite a high value of 0.5 mol% based on the olefin. With a reaction-time of 4 h and a selectivity of 89%, this catalytic system can be considered as highly reactive and highly selective.

Performing the reaction in propylene carbonate instead of toluene rises the selectivity to *n*-nonanal from 89 up to 95%. This solvent has not only an influence on the selectivity but offers in addition the opportunity to recover the catalyst in a two-phase fluid–fluid system. In five recycling runs the catalytic phase could be reused without any loss of activity and selectivity to *n*-nonanal. The resulting total turnover number had a value of 866 while the turnover frequency was 34 h<sup>-1</sup>.

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**Keywords:** Isomerization–hydroformylation; Homogeneous catalysis; Internal olefin; Rhodium; BIPHEPHOS

## 1. Introduction

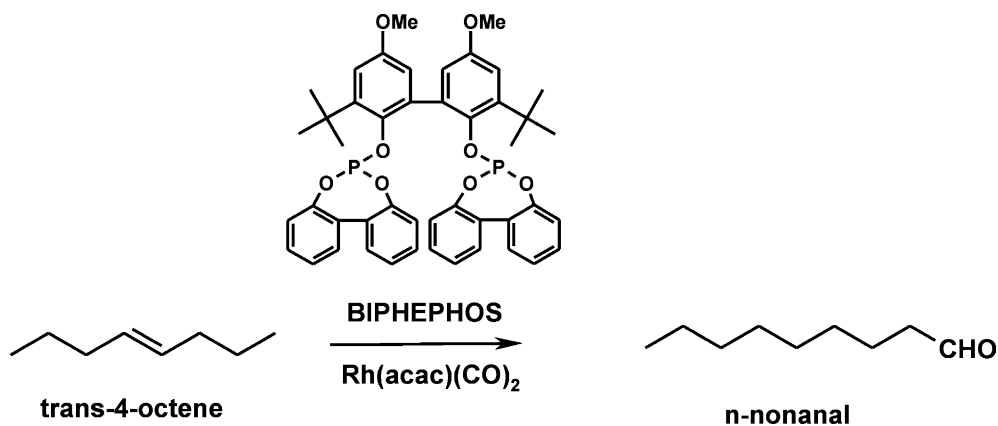
The transition metal catalyzed hydroformylation of aliphatic olefins is an important reaction in industrial chemistry [1]. Usually the hydroformylation is carried out as a homogeneous reaction with cobalt or rhodium-based catalysts. The advantages of the rhodium-systems are the milder reaction conditions, the higher (*n*:*i*) ratio of the products and the higher activity [2].

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In general, the linear aldehydes are the desired species to be formed, because of their high-potential consecutive chemistry. For example, the aldehydes that can be oxidized to the corresponding acids or hydrogenated to the alcohols which are valuable starting materials for the synthesis of polymer plasticizers. The great importance of the “oxo-products” is impressively illustrated by the world-consumption of more than 6.1 million tons per year.

In the last few years, the hydroformylation of mixtures of long-chain and branched olefins, such as a mixture of isomeric octenes to C<sub>9</sub>-aldehydes has



Scheme 1. Hydroformylation of *trans*-4-octene with a rhodium-BIPHEPHOS catalyst.

caused great attention because high performance plasticizers, such as di-*iso*-nonyl phthalate (DINP) have been requested with the development of the plastic industries [3].

To improve the regioselectivity of the hydroformylation, the use of phosphorus ligands has been established [4–6]. For example, Beller et al. published the hydroformylation of 2-pentene to C<sub>6</sub>-aldehydes with a rhodium/NAPHOS catalyst resulting in an amazing regioselectivity of 90% to the linear aldehyde [7].

In our work, we investigated the hydroformylation of *trans*-4-octene to C<sub>9</sub>-aldehydes with a catalyst consisting of Rh(acac)(CO)<sub>2</sub> and the chelating phosphite ligand BIPHEPHOS (Scheme 1). This ligand was designed to enhance the regioselectivity in the hydroformylation of propene and was patented by Union Carbide Cooperation (UCC) already in 1980s [8,9]. To the best of our knowledge, it has not been used in the hydroformylation of internal olefins like *trans*-4-octene.

## 2. Experimental

### 2.1. Reagents

*trans*-4-Octene was purchased from Sigma–Aldrich (purity >90%) and was used without any purification steps. The solvent toluene (p.a.) was purchased from Acros–Organics. The catalyst precursor Rh(acac)(CO)<sub>2</sub> was received from OMG AG and Co. KG and the syngas (CO:H<sub>2</sub> = 1:1, purity > 99.9%)

from BASF. The synthesis of the chelating phosphite ligand BIPHEPHOS was carried out according to the works of Hewgill and Hewitt [10], Cuny and Buchwald [11] and Butsugan et al. [12]. The constant purity of the prepared ligand charges was proved by NMR methods (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR). The spectroscopic data were the same as in [11].

### 2.2. General procedure of hydroformylation experiments

All hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA), however, a modified vessel with a volume of 70 ml was used. The reaction mixture was transferred into the reactor using standard “Schlenk-technique” to prevent oxidation of the catalyst precursors as well as other deleterious reactions.

In a typical experiment 13 mg (0.05 mmol) Rh(acac)(CO)<sub>2</sub>, 120 mg (0.15 mmol) BIPHEPHOS and 1200 mg (9.7 mmol) *trans*-4-octene were dissolved in 20 ml of toluene. Then, the solution is transferred into the evacuated stainless steel autoclave. The vessel was heated to reaction temperature and then pressurized to the desired syngas pressure. After heating up in about 45 min, the stirrer was accelerated from 50 to 500 rpm. Four hours after loading with syngas the vessel was cooled down to room temperature and excess syngas was expanded into the hood. The product was separated from the catalyst by vacuum distillation. A product sample was analyzed using a

calibrated gas chromatograph (Innowax-column) with dodecane as internal standard and toluene as solvent. Reaction products were identified by GC/MS,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

### 3. Results and discussion

#### 3.1. Variation of temperature

To find the reaction temperature at which the consecutive processes of isomerization and hydroformylation take place with both an acceptable velocity and an optimum selectivity to *n*-nonanal, the temperature range from 80–150 °C was investigated. The concentration of the catalyst precursor ( $\text{Rh}(\text{acac})(\text{CO})_2$ ) was 0.5 mol% based on *trans*-4-octene. The rhodium compound, the threefold amount of BIPHEPHOS and *trans*-4-octene were dissolved in toluene and 20 bar of syngas were pressurized to the reactor after the desired reaction temperature was reached.

The results of the conversion of *trans*-4-octene and the yield of *n*-nonanal are shown in Fig. 1. At moderate temperatures between 80 and 100 °C the conversion of *trans*-4-octene and the yield of *n*-nonanal are quite low. At temperatures higher than 130 °C, the yield of *n*-nonanal increases and the gap between the conversion of *trans*-4-octene and the yield of the linear aldehyde becomes bigger due to increasing hydrogenation of octene to octane. Hence, the optimum reaction temperature lies near 120 °C, where the reactivity is already quite high, but the selectivity to *n*-nonanal is still favourable.

#### 3.2. Variation of phosphorus:rhodium ratio

To investigate the influence of the amount of the ligand BIPHEPHOS, the phosphorus:rhodium ratio was varied in the range of 0–10 (see Fig. 2). Already a (P:Rh) ratio of 3:1 leads to the quite high yield of *n*-nonanal of more than 60%. Going on to higher (P:Rh) ratios does not have any significant influence concerning the yield of the linear aldehyde. If there is no phosphorus in the reaction mixture at all, only a yield of 20% *n*-nonanal is observed.

#### 3.3. Variation of rhodium concentration and optimization of reaction time

To study the influence of the catalyst concentration, reactions were carried out with rhodium concentrations of 0,10, 0.25 and 0.50 mol% based on *trans*-4-octene. The results in Table 1 show, that the conversion of *trans*-4-octene as well as the yield of *n*-nonanal are strongly dependant on the rhodium concentration.

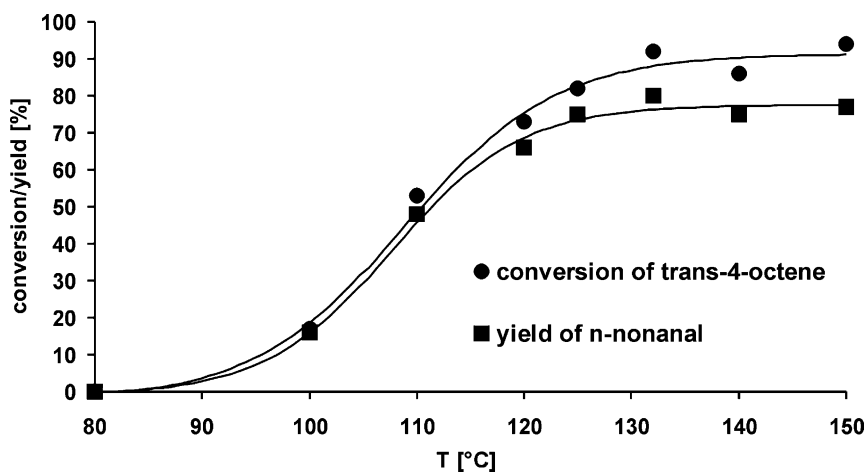


Fig. 1. Variation of the reaction temperature. Constant reaction conditions: 0.5 mol%  $\text{Rh}(\text{acac})(\text{CO})_2$ , P:Rh = 6:1,  $p(\text{CO}/\text{H}_2) = 20$  bar, 1.2 g *trans*-4-octene, 20 ml toluene,  $t = 4$  h.

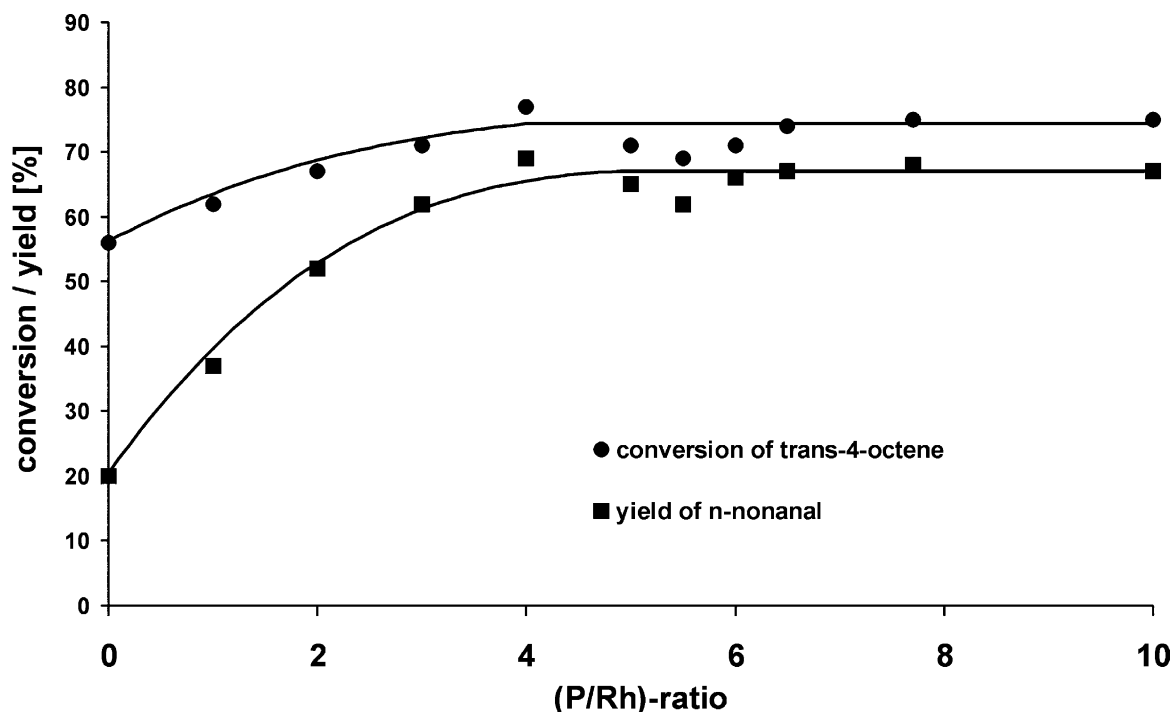


Fig. 2. Influence of the (P/Rh) ratio on conversion and yield. Constant reaction conditions: 0.5 mol% Rh(acac)(CO)<sub>2</sub>,  $T = 125^{\circ}\text{C}$ ,  $p(\text{CO}/\text{H}_2) = 20$  bar, 1.2 g *trans*-4-octene, 20 ml toluene,  $t = 4$  h.

Two kinetic investigations were carried out at  $115^{\circ}\text{C}$  and  $125^{\circ}\text{C}$  (see Fig. 3) with a rhodium concentration of 0.5 mol% based on the *trans*-4-octene. The two curves differ evidently concerning the reaction velocity: at the higher temperature of  $125^{\circ}\text{C}$  the reaction is finished after 4 h, while at the lower temperature of  $115^{\circ}\text{C}$  it takes 2 h longer to reach the same yield of *n*-nonanal of 89%. At both temperatures the formation of 3% octane is observed due to the hydrogenation of *trans*-4-octene to the saturated hydrocarbon.

Table 1  
Variation of the rhodium concentration<sup>a</sup>

Rhodium concentration (mol%)	Conversion <i>trans</i> -4-octene (%)	Yield <i>n</i> -nonanal (%)
0.10	86	29
0.25	85	65
0.50	82	75

<sup>a</sup> Constant reaction conditions: P:Rh = 6:1,  $T = 125^{\circ}\text{C}$ ,  $p(\text{CO}/\text{H}_2) = 20$  bar, 1.2 g *trans*-4-octene, 20 ml toluene,  $t = 4$  h.

### 3.4. Reaction in propylene carbonate

Propylene carbonate represents a medium-polar organic solvent which can be used in liquid–liquid two-phase reaction systems [13–15]. Using this solvent, the optimized reaction parameters were a catalyst concentration of 0.5 mol% Rh(acac)(CO)<sub>2</sub> based on the olefin, a P:Rh ratio of 10:1, a syngas pressure of 10 bar, a temperature of  $125^{\circ}\text{C}$  and a reaction time of 4 h. Performing the reaction with these parameters leads to a conversion of *trans*-4-octene of 94% and a selectivity to *n*-nonanal of 95%. Only very few amounts of the branched aldehydes and the hydrogenation product octane (together less than 5%) are formed. In comparison to the reaction in toluene this is a remarkable enhancement which can be explained by the low solubility of the olefin in the propylene carbonate phase. This dilution of the olefin (solubility of *trans*-4-octene in propylene carbonate is 2.5 wt.% at ambient temperature) affects a further deceleration of the reaction velocity

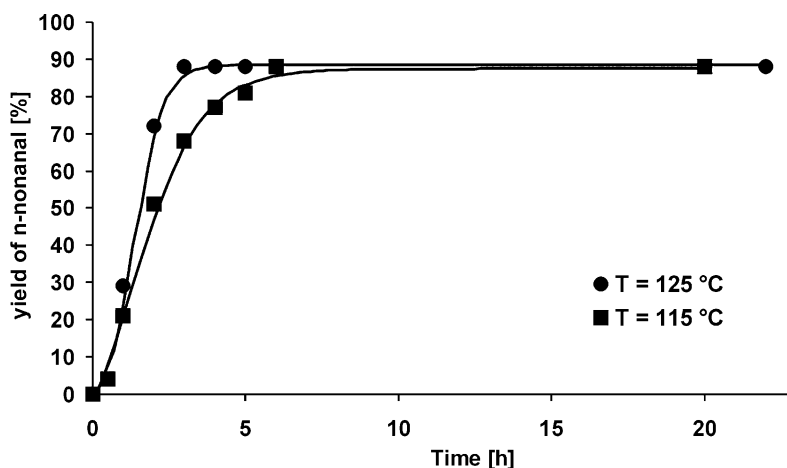


Fig. 3. Influence of the reaction time on conversion and yield. Constant reaction conditions: 0.5 mol% Rh(acac)(CO)<sub>2</sub>, P:Rh = 6:1,  $T = 115$  and  $125\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}/\text{H}_2) = 20$  bar, 1.2 g *trans*-4-octene, 20 ml toluene.

resulting in an amazing selectivity to *n*-nonanal of 95%.

To investigate the long-time stability of the catalytic system a sequence of five reactions with the same propylene carbonate phase was carried out. In each run an amount of 1.2 g of *trans*-4-octene was added. Both the conversion of *trans*-4-octene and the selectivity to *n*-nonanal proved to remain at the same high levels during all successive experiments (see Fig. 4). After these experiments the *n*-nonanal was extracted by the use of dodecane as solvent. No <sup>31</sup>P

NMR signals were observed in the dodecane phases, which remained colourless after the extraction of the aldehyde.

In the reaction system of propylene carbonate the turnover frequency had a value of  $34\text{ h}^{-1}$  resulting in a total turnover number of 866 after five runs. These values were determined after the whole amount of the olefin was converted to aldehydes. Otherwise the determination of the conversion of the olefin in this two-phase liquid system is not accurate enough to calculate a reliable TOF value.

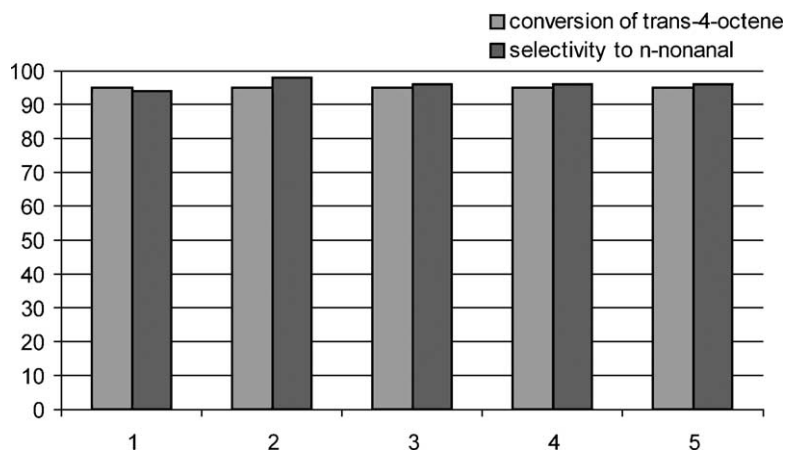


Fig. 4. Longtime stability of the catalytic phase. Constant reaction conditions: 0.5 mol% Rh(acac)(CO)<sub>2</sub>, P:Rh = 10:1,  $T = 125\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}/\text{H}_2) = 10$  bar, 1.2 g *trans*-4-octene for each run, 20 ml propylene carbonate.

#### 4. Conclusions

The hydroformylation of the internal olefin *trans*-4-octene to *n*-nonanal using toluene as solvent could be carried out with good yields up to 88%. At a temperature of 125 °C the reaction proved to be quite slow (4 h, TOF = 46 h<sup>-1</sup>) but very selective.

In comparison to the literature results [7] (TOF = 43 h<sup>-1</sup>, selectivity to *n*-nonanal = 70%), the rhodium-BIPHEPHOS catalyst has nearly the same activity, but a higher selectivity to *n*-nonanal of 89%.

Performing the reaction in propylene carbonate reveals a significant influence on the selectivity, reaching a value of 95% of *n*-nonanal (TOF = 34 h<sup>-1</sup>, TON = 866). The catalyst accelerates the isomerization of the olefin due to the high rhodium concentration which results in a higher linearity of the aldehydes.

In the next step of our investigations we will study the recycling of the rhodium catalyst especially by use of the liquid–liquid two-phase technique.

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