

Homogeneous and heterogeneous catalyzed three-step synthesis of 2-ethylheptanoic acid from carbon dioxide, butadiene and hydrogen

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Received 19 November 2001; accepted 19 April 2002

Abstract

This paper describes the synthesis of 2-ethylheptanoic acid (**2**) by hydrogenation of the δ -lactone (**1**), which is on his part very well available by the reaction of butadiene with carbon dioxide. A two-step hydrogenation process was found to be the most successful reaction pathway. First of all the cleavage of the δ -lactone ring is applied. This process involves a homogeneously catalyzed two-phase hydrogenation with a water-soluble in situ rhodium-phosphine catalyst. The effects of ligand, temperature, hydrogen pressure and catalyst concentration have been examined. The catalyst containing aqueous phase has been recycled five times without loss of activity. The leaching of the rhodium into the organic phase was measured and found to be in the range of 1 wt.% of the starting catalyst concentration. The hydrogenation of the remaining double bonds was carried out with a heterogeneous palladium/charcoal catalyst in methanol.

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Keywords: Hydrogenation; Homogeneous catalysis; Biphasic catalysis; Carbon dioxide; Lactone

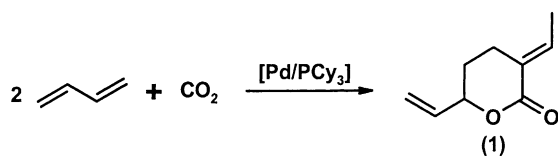
1. Introduction

The palladium-catalyzed co-oligomerization of 1,3-butadiene and carbon dioxide (**Scheme 1**) is one of the few successful examples of C–C bond forming reactions of CO₂. Since its discovery in 1976 by Inoue et al. [1], this reaction has been extensively studied on the influence of the catalysts, ligands and solvents. Behr et al. [2,4] and Behr and Juszak [3] have improved the co-oligomerization towards the formation of the δ -lactone (**1**) allowing its preparation in multi-kilogram scale and with selectivities up to 95%.

An industrial application of this process can only be realized if the recycling of the homogeneously dissolved palladium catalyst is guaranteed. Two different approaches have been published dealing with this subject. Dinjus and co-workers [5,6] and Holzhey and Pitter [7] describe the immobilization of the catalyst consisting of a palladium(II) precursor on a polymer-bound phosphine. By our group a process for the production of (**1**) is investigated in a continuous miniplant. The recycling of the catalyst has been realized completely by an extraction unit [8].

The industrial value of δ -lactone (**1**) as intermediate product is till now very low because only a few successful consecutive reactions are described, e.g. the synthesis of 2-ethylidene-5-hydroxy-6-heptenoic acid and some derivatives [9]. Dinjus and co-workers [10] report the synthesis of polymers with an intact lactone

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PCy₃: Tricyclohexylphosphine

Scheme 1. Preparation of δ -lactone (**1**).

ring structure in the main chain based on (**1**). Nevertheless, these products have not found great interest in industry due to a complicated synthesis or isomeric mixtures.

We would like to describe a new catalytic three-step synthesis of 2-ethylheptanoic acid (**2**) that could be used for many applications, e.g. in alkyd resins, lubricants, or as stabilizer for PVC. Furthermore, 2-ethylheptanoic acid is a possible intermediate for the production of solvents and softeners.

2. Experimental

2.1. Reagents

The δ -lactone was synthesized according to the instructions in [11]. Triphenylphosphine trisulfonate sodium salt (TPPTS, Scheme 7) was used as a 26 wt.% aqueous solution, which was supplied by Celanese AG. All metals and catalysts were used as received from Degussa AG without further purification. Hydrogen 3.0 supplied from Messer–Griesheim was used. All solvents were degasified and used saturated with argon. All reactions and handling were done under argon using standard Schlenk tube techniques.

2.2. Homogeneous hydrogenation

In a typical experiment, 38 mg (1.48×10^{-4} mol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 3.31 g (1.48×10^{-3} mol) aqueous solution of TPPTS, 12.17 g of water and 15 g (0.1 mol) of δ -lactone (**1**) were weighed in a Schlenk tube and transferred into an evacuated 67 ml stainless steel autoclave. The vessel was heated up to reaction temperature, pressurized with 10 bar hydrogen and the reaction started by accelerating the stirrer velocity to 1000 rpm. In regular intervals, liquid samples were taken from the organic phase. For the sampling the stirrer was stopped for 1 min to allow phase separation.

All recycling experiments and long-term experiments were done in a 300 ml stainless steel autoclave with 75 g (0.49 mol) of δ -lactone and the appropriate other weighed portions.

2.3. Heterogeneous hydrogenation

A typical procedure for a heterogeneous hydrogenation is as follows: a 300 ml stainless steel autoclave was charged under argon with 10 g (0.066 mol) δ -lactone (**1**), 0.25 g palladium on charcoal (5% Pd) and 90 ml methanol. The vessel was heated up to reaction temperature, pressurized with hydrogen and then the reaction started by accelerating the stirrer velocity at 700 rpm and held constant for 1 h. After cooling to ambient temperature, the remaining gas was vented from the reactor and the catalyst was removed by filtration off the reaction mixture.

2.4. Analysis and product characterization

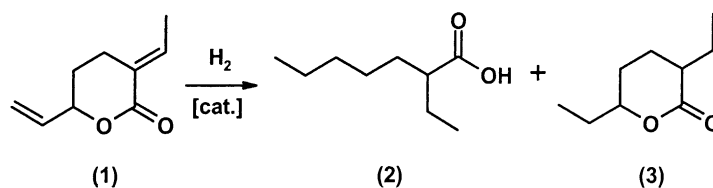
All reaction mixtures were analyzed by gas chromatography using undecylacetate as an internal standard. Separation of isomeric mixtures was realized by preparative gas chromatography. The characterization of new substances was done by standard NMR-experiments (¹H, ¹³C, COSY, NOESY). Water contents were determined by Karl Fischer titration. Rhodium contents were measured using inductively coupled plasma (ICP).

3. Results and discussion

3.1. Heterogeneous hydrogenation of the δ -lactone (**1**)

In the heterogeneous hydrogenation of the δ -lactone (**1**), besides the desired product 2-ethylheptanoic acid (**2**), the formation of saturated, isomeric δ -lactones (**3**) is observed (see Scheme 2). These compounds differ in the position of the hydrogen atoms in positions 2 and 5 proved by NOESY experiments of the pure compounds.

Variation of the solvent, the concentration of the catalyst, temperature and hydrogen pressure changes the selectivity of this reaction. The results of the heterogeneous hydrogenations are summarized in Table 1.



Scheme 2. Heterogeneous hydrogenation.

The highest yield of 2-ethylheptanoic acid (**2**) in heterogeneous hydrogenation is achieved using methanol as solvent. Nevertheless, a yield of 28% is rather low. Using non-polar solvents, like *n*-heptane, the formation of the isomeric, saturated δ -lactones (**3**) is enhanced. Selectivities up to 95% are possible. If an isomeric mixture of (**3**) is hydrogenated under the same conditions no more cleavage of the lactone ring is observed. Therefore, a quantitative production of 2-ethylheptanoic acid via heterogeneous catalysis was not achieved.

3.2. Homogeneous biphasic hydrogenation of the δ -lactone

Applying standard monophasic homogeneous hydrogenation catalysts in this reaction, e.g. Wilkinson's catalyst $\text{ClRh}(\text{PPh}_3)_3$, the same product distribution as for the heterogeneously catalyzed hydrogenation is observed.

When a biphasic hydrogenation is carried out in presence of a water-soluble in situ rhodium-TPPTS catalyst an exothermic reaction takes place, and 2-ethylheptanoic acid (**2**) is formed as main product. After a reaction time of 4 h, the yield of 2-ethylheptanoic acid is about 63%. The intermediates in this

reaction are exclusively isomeric C_9 -carboxylic acids differing only in the number and position of the remaining double bonds. The different isomers (**4–9**) were identified by NMR analysis (see Scheme 3). Neither any saturated nor partially hydrogenated lactones are observed.

It can be concluded, that under homogeneously catalyzed, two-phase reaction conditions the cleavage of the lactone ring is much faster than the hydrogenation of the two double bonds. If saturated lactones, like (**3**) are hydrogenated under the same two-phase reaction conditions no reaction is observed. The reaction can only take place if the coordination of the lactone with the catalytic complex is achieved, i.e. the double bonds are essential. This point will now be discussed in detail based on the postulated catalytic cycle.

3.2.1. Mechanism

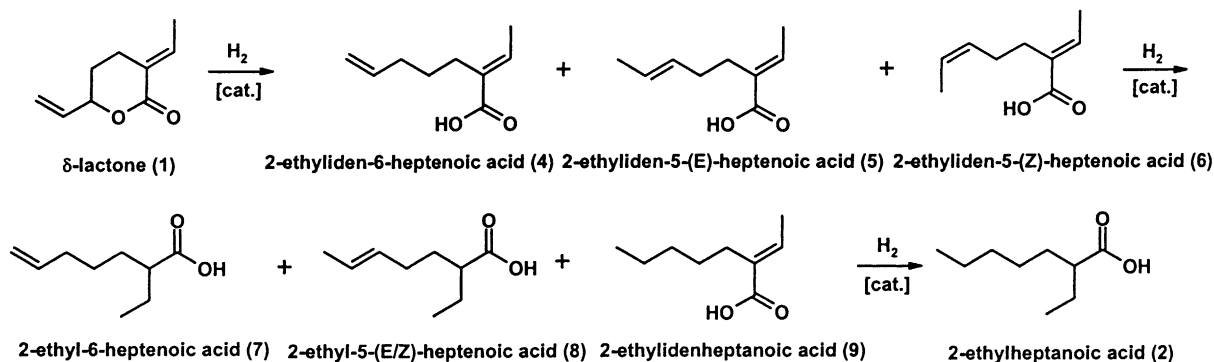
The progress of the reaction was investigated in a long-term experiment and the results clearly prove a consecutive reaction, shown in Scheme 3. Additionally, an isomerization of the double bonds was observed (see Fig. 1).

First of all the lactone ring opens and isomerizations occur that lead to a reaction mixture containing the three isomers (**4–6**). Then consecutively one of the

Table 1
Results of the heterogeneous hydrogenation of δ -lactone (**1**)

Number	Catalyst Pd/C (g)	Catalyst Pd/C, Pd (mol%)	Pressure (bar H_2)	Solvent	Products		
					δ -Lactone (1)	(2)	(3)
1	0.25	0.27	10	Methanol	0	28	72
2	0.25	0.27	10	THF	0	16	84
3	0.25	0.27	10	<i>n</i> -Heptane	0	17	83
4	0.05	0.05	10	THF	0	5	95
5	0.025	0.01	10	THF	61	0	39
6	0.05	0.05	5	THF	54	0	46

Conditions: $m(\delta\text{-lactone}) = 10 \text{ g}$, $V(\text{solvent}) = 90 \text{ ml}$, $t = 60 \text{ min}$, $T = 60^\circ\text{C}$, catalyst: Pd/C (5–10% Pd), stirrer velocity = 700 rpm.



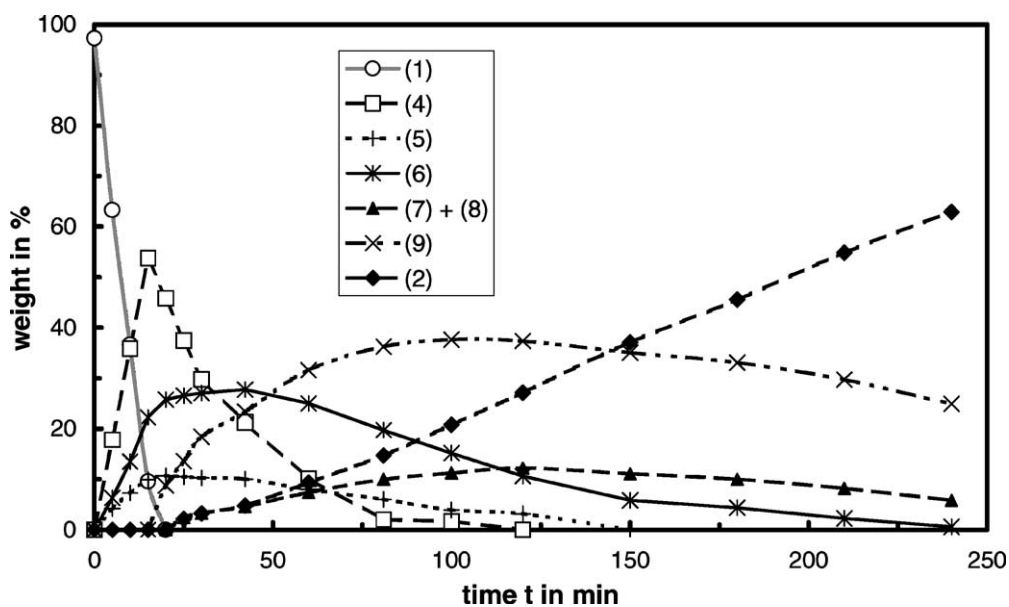
Scheme 3. Homogeneous biphasic hydrogenation.

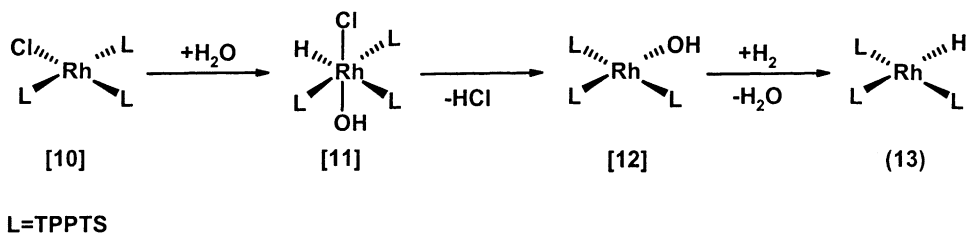
remaining double bonds is hydrogenated to the single unsaturated isomeric acids (7–9) and finally to the product (2). Based on these studies, we propose a catalytic cycle, that explains the observed product distribution. First of all the catalytic active species has to be formed, which is described in Scheme 4.

Dissolving TPPTS and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in water lead to compound (10). Kulpe [12] describes the formation of complex (11) by addition of a molecule H_2O and by abstraction of HCl the hydroxy-complex (12) is generated. In our opinion, the active catalyst consists

of a hydrido-TPPTS species (13), although there is no experimental proof till now. The chloro-complex (11) as well as the hydroxy-complex (13) would not give the octahedral rhodium complex (15), which is essential for the product formation. If complex (15) possessed a chloro, respectively hydroxy ligand, the product would be a monosubstituted carboxylic acid, which is not observed. The whole catalytic cycle is shown in Scheme 5.

First, the active species (13) associates a molecule of δ -lactone (1) with the terminal double bond giving

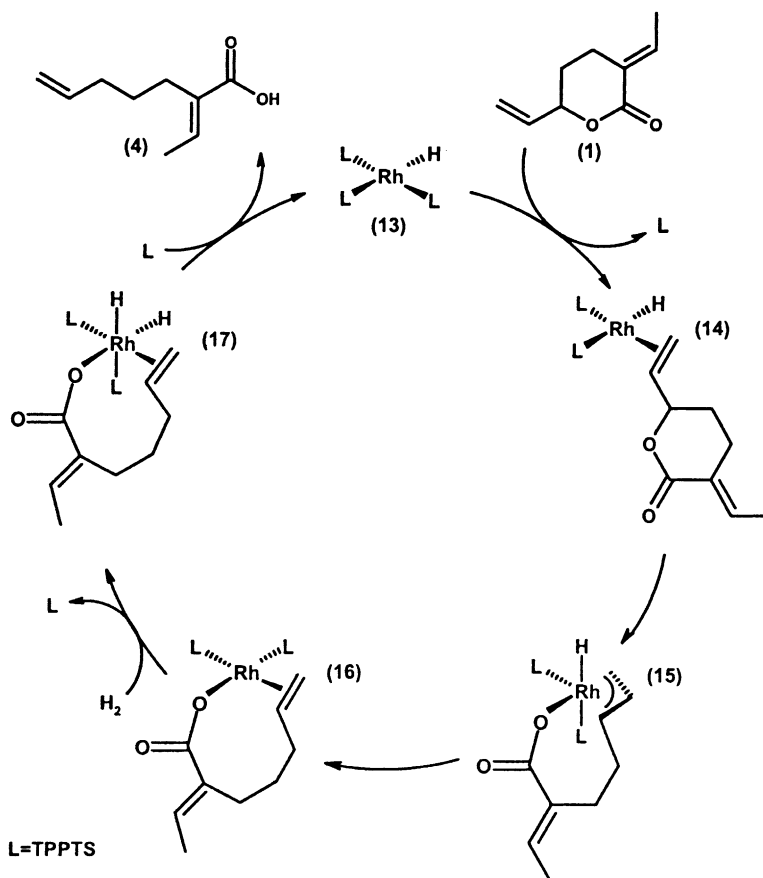
Fig. 1. Conversion of δ -lactone to isomeric C₉-carboxylic acids.

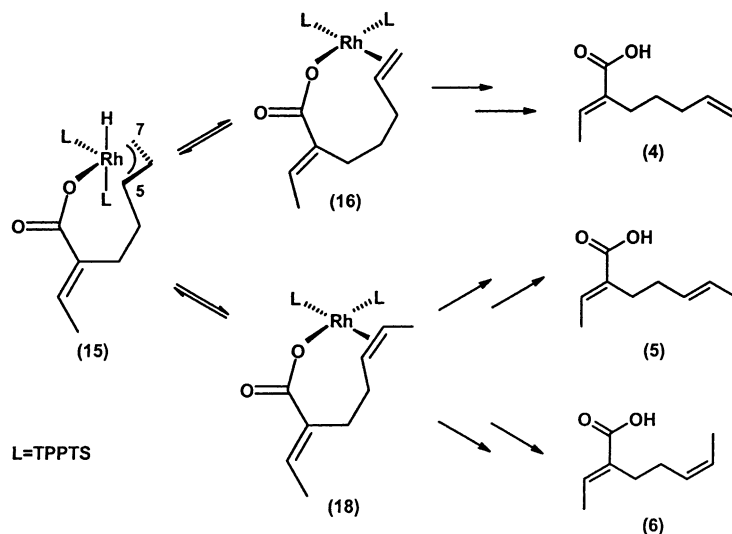


Scheme 4. Possible formation of the catalytic active species.

complex (14). Then an allylic substitution takes place causing the opening of the lactone ring. In detail, the steps are the formation of an η^3 -allyl-carboxylate–rhodium complex by oxidative addition of the lactone (15). Already in 1986, Behr et al. postulated that this kind of complexes play an important role in

lactone formation [13]. A reductive elimination of the hydrogen and the allyl ligand leads to the 16 electron carboxylate–olefin complex (16). In a further oxidative addition step hydrogen is added releasing one ligand TPPTS. The resulting species eliminates the product (4), and the addition of the ligand TPPTS regenerates

Scheme 5. Model of the catalytic cycle for the homogeneously catalyzed, biphasic hydrogenation of δ -lactone.



Scheme 6. Isomerization due to different reaction pathways.

again the starting compound (**13**) of the catalytic cycle.

Using this catalytic cycle, it is also possible to explain the isomerization reactions, which is illustrated in Scheme 6.

According to Scheme 6, there are two possibilities for the reductive elimination of complex (**15**): insertion of hydrogen in position 5 of the carboxylate ligand or at the end of the chain at position 7. Insertion in position 5 gives the carboxylic acid with the terminal double bond (**4**). The second possibility, insertion at position 7, leads to a mixture of the (*E*) and (*Z*)—isomer of the carboxylic acids (**5**) and (**6**) with double bonds at positions 2 and 5.

The hydrogenation of the remaining double bonds follows the generally accepted mechanism for rhodium catalyzed reactions [14].

3.2.2. Optimization

The homogeneously catalyzed biphasic hydrogenation was optimized with respect to temperature, hydrogen pressure, stirring velocity, catalyst and ligand concentration. A typical plot of the remaining δ -lactone concentrations with respect to the temperature is shown in Fig. 2.

The results in this figure indicate that a total conversion of the δ -lactone can already be obtained after 20 min at a reaction temperature of 90 °C.

The influences of the different parameters are discussed on the basis of the first sample of each experiment taken after 5 min. The results are summarized in Table 2. After 60 min in all experiments, the conversion of the δ -lactone is complete. The turnover frequency [$n(\text{product})/(n(\text{Rh}) \times \text{time})$] is calculated after 5 min referring to 1 h.

3.2.2.1. Effect of the temperature. The reaction rate depends strongly on the temperature. An increase of the temperature of 10 °C leads to higher TOFs of more than 1000 (Table 2, nos. 1–3). The highest temperature that can be applied to this reaction is about 125 °C. At higher temperatures, the deactivation of the catalyst begins turning the color of the catalyst phase from orange/red to brown/black.

3.2.2.2. Effect of the hydrogen pressure. The effect of the hydrogen pressure is rather small (Table 2, nos. 2, 4 and 5). The increase of the reaction rate will not compensate the higher costs for a reaction unit for higher pressure ranges in a potential future plant.

3.2.2.3. Effect of the stirrer velocity. The TOF (and that means the reaction rate) increases at higher stirring velocities (Table 2, nos. 2, 6–8). This indicates limitations due to mass transport problems, a common subject in two-phase liquid–liquid reactions.

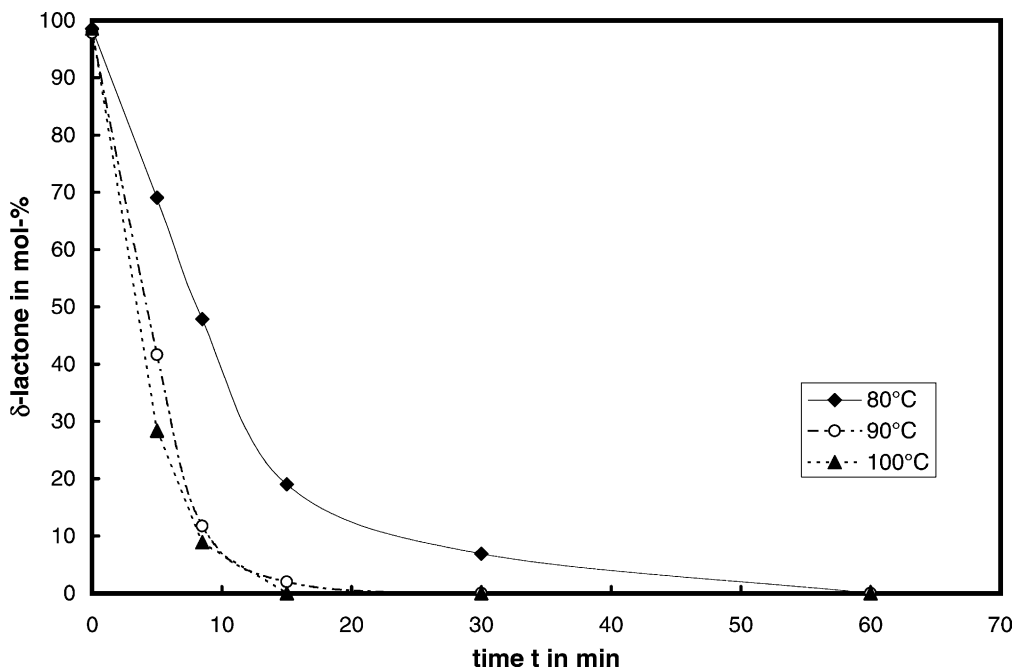


Fig. 2. Typical reaction plot of the homogeneous, biphasic hydrogenation of δ -lactone with respect to temperature.

3.2.2.4. Variation of the phosphorus/rhodium ratio.

Increasing the P/Rh ratio, the reaction rate increases (Table 2, nos. 2, 9 and 10). Presumably, the active catalyst consists of a rhodium central atom modified with several ligands. If the amount of ligands raises, the number of active species will raise, too.

Furthermore, an excess of polar ligands prevents the leaching of rhodium into the organic phase.

3.2.2.5. Influence of the amount of catalyst.

The influence of the amount of catalyst was investigated in the range from 250–1500 ppm rhodium referring to

Table 2
Results of the homogeneous, biphasic hydrogenation of δ -lactone

Number	Temperature (°C)	Pressure (bar H ₂)	Stirring velocity (rpm)	P/Rh (mol/mol)	Weight catalyst (ppm)	Conversion δ -lactone in percent (after 5 min)	TOF (h ⁻¹) (after 5 min)
1	80	10	1000	10	1000	31	2453
2	90	10	1000	10	1000	58	4586
3	100	10	1000	10	1000	72	5837
4	90	20	1000	10	1000	55	4340
5	90	30	1000	10	1000	65	5173
6	90	10	600	10	1000	40	3328
7	90	10	800	10	1000	44	3725
8	90	10	1200	10	1000	75	6261
9	90	10	1000	5	1000	37	2773
10	90	10	1000	20	1000	69	5423
11	90	10	1000	10	250	20	5618
12	90	10	1000	10	500	56	8784
13	90	10	1000	10	1500	85	4573

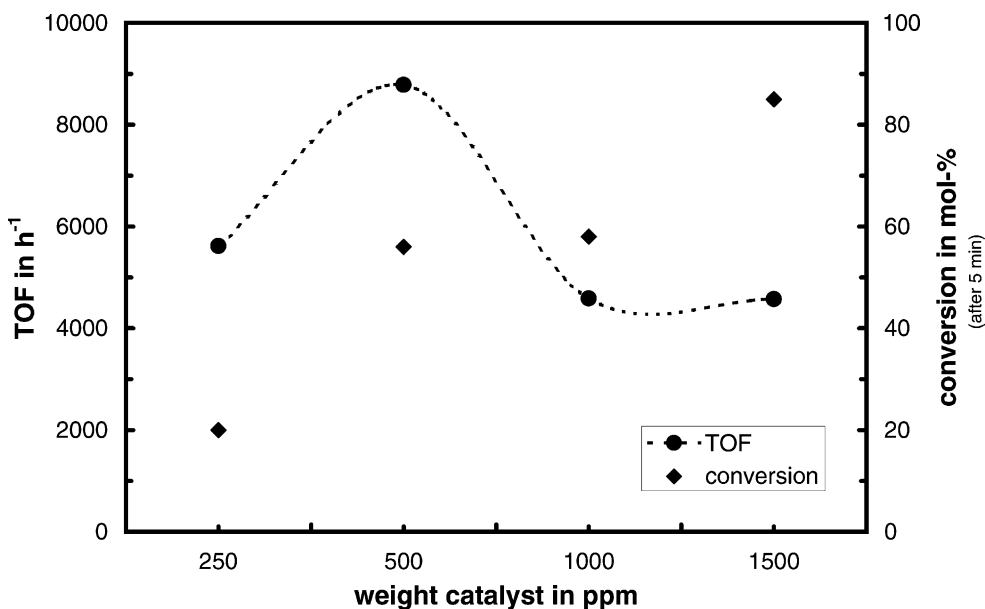


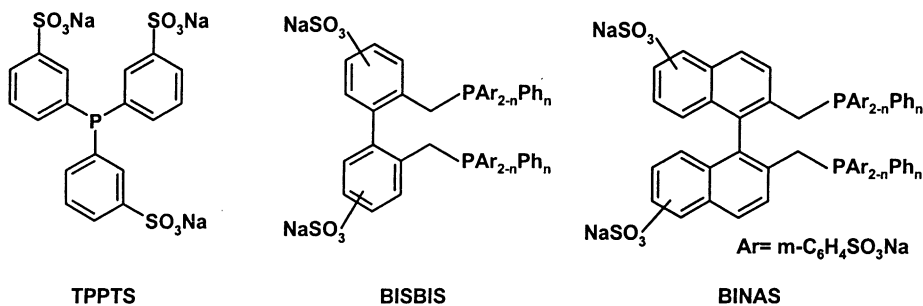
Fig. 3. Influence of the amount of catalyst referring to conversion and TOF.

the amount of δ -lactone used (Table 2, nos. 2, 11–13). The results are given in Fig. 3.

As expected the conversion (after 5 min) increases with increasing amount of catalyst. The number of active catalyst species is higher and therefore a greater number of molecules are converted simultaneously. At 500 ppm, the TOF reaches a maximum. At higher catalyst concentrations the conversion of the δ -lactone (after 5 min) is already advanced and only a small part of the active catalyst species are used for the allylic substitution reaction. Hence, reasonable reaction times are possible with catalyst concentrations of less

than 500 ppm, higher catalyst concentrations are not necessary.

3.2.2.6. *Ligand variation.* Besides TPPTS, the water-soluble chelating diphosphines BINAS (sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl) and BISBIS (sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl), whose structures are shown in Scheme 7, are often employed in the homogeneous, two-phase hydrogenation. The results of the hydrogenation of δ -lactone (**1**) are summarized in Table 3.



Scheme 7. Ligands used for the homogeneously catalyzed, biphasic hydrogenation.

Table 3

Application of different water-soluble ligands in the homogeneous, biphasic hydrogenation of δ -lactone (**1**)

Number	Ligand	P/Rh-ratio (mol/mol)	Weight rhodium (ppm)	Conversion δ -lactone in percent (after 5 min)	TOF (h^{-1}) (after 5 min)
12	TPPTS	10	500	56	8784
14	BINAS	20	500	40	6039
15	BISBIS	20	500	26	3764

Conditions: $T = 90^\circ\text{C}$, $p = 10$ bar H_2 , stirring velocity = 1000 rpm.

There is no change in selectivity using BINAS or BISBIS. The mechanism of the reaction does not change, isomerizations occur in the same way. However, the reaction rate compared to TPPTS decreases. The main advantage of these chelating diphosphines, e.g. in hydroformylations [15] is a higher regio-selectivity to the desired product. Because the hydrogenation of the δ -lactone (**1**) leads only to one product there is no need to use the more expensive ligands BINAS or BISBIS.

3.2.3. Recycling of the homogeneous catalyst

Two test series were carried out to recycle the homogeneous water-soluble catalyst. The recycling was realized by phase separation in a separating funnel. Afterwards, the catalyst containing aqueous phase was retransferred in the autoclave and reused for the next reaction.

3.2.3.1. Recycling experiments under adiabatic conditions. The experiments were started at a reaction temperature of 90°C and the catalyst was used five times. The results are summarized in Table 4. T_{max} indicates the highest temperature achieved in each experiment. After phase separation the water content as well as the rhodium content of the organic phase were measured.

In the initial run, the conversion of the δ -lactone (**1**) is incomplete. In the first recycling run, the reaction rate increases effecting a complete conversion and even the formation of 10% of the totally hydrogenated product 2-ethylheptanoic acid (**2**) is observed. In the second recycle run, the reaction temperature exceeds to 130°C causing the catalyst to decay partially. The solubility of the rhodium in the organic phase can be related to its water content. In Fig. 4, the measured Rh leaching is compared to the calculated Rh content of the organic phase.

Based on the assumption that the concentration of rhodium in the water dissolved in the organic phase is equal to its concentration in the aqueous phase, it can be concluded that the rhodium leaching is caused by the solubility of the aqueous phase in the product (organic phase).

3.2.3.2. Recycling experiments under isothermal conditions. In a second test series (see Table 5), a cooling coil in the autoclave was used to keep the temperature in the vessel constant at 110°C . Because of the incomplete conversion of the δ -lactone in the first test series, the catalyst formation was given 45 min to proceed at 110°C and 10 bar hydrogen pressure. After this time the δ -lactone (**1**) was added and the reaction was started.

Table 4

Recycling of the homogeneous catalyst under adiabatic conditions

Number	T_{max} ($^\circ\text{C}$)	Conversion δ -lactone (%)	Yield (4-9) (%)	Yield (2) (%)	Water in organic phase (%)	Weight Rh in organic phase ($\mu\text{g/g}$)	TOF (h^{-1}) (after 5 min)	TON
1	96	92	92	0	0.78	7.6	3286	623
2	122	100	90	10	0.62	5.6	9931	1300
3	131	100	84	16	0.76	9.2	9858	1978
4	122	100	87	13	0.79	10.4	6042	2655
5	119	100	90	10	1.00	10.4	5551	3332

Conditions: $p = 10$ bar H_2 , stirrer velocity = 1000 rpm, $m(\delta\text{-lactone}) = 75$ g, $m(\text{Rh}) = 1000$ ppm, $t = 30$ min, $n(\text{P})/n(\text{Rh}) = 10 : 1$.

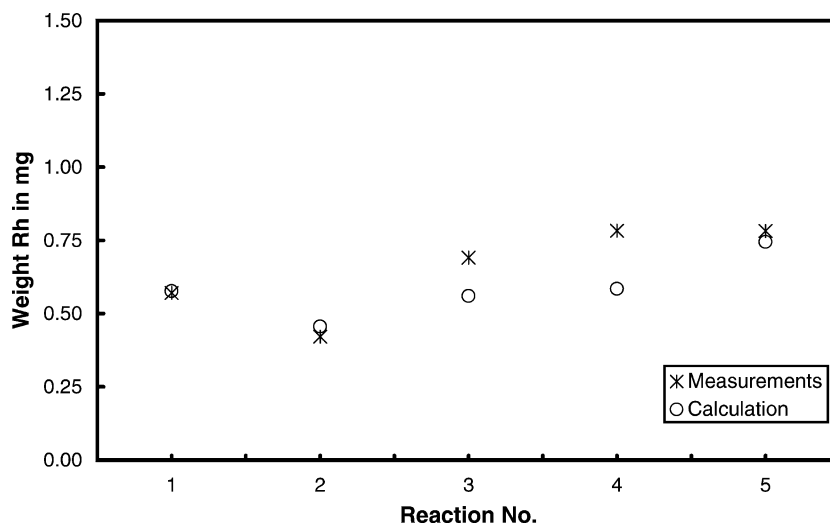


Fig. 4. Comparison of the rhodium concentration measured vs. calculated.

Preforming of the catalyst had no effect on the reaction rate, because the conversion of the initial run was still incomplete. Probably the active species is not generated until the reactant, the δ -lactone, is present. Since the first recycling run the catalyst performs well and in the following five runs complete conversions are obtained without any tendency of catalyst deactivation. Overall 435 g δ -lactone (**1**) have been converted selectively with only 38 mg rhodium to a mixture of the isomeric, unsaturated 2-ethylidene-heptenoic acids (**4–9**).

3.3. Heterogeneous hydrogenation of the isomeric mixture (**4–9**)

The homogeneous, biphasic hydrogenation of δ -lactone (**1**) leads to the corresponding isomeric mix-

Table 5
Recycling of the homogeneous catalyst under isothermal conditions

Number	Conversion δ -lactone (%)	TON
1	78	1062
2	100	2417
3	100	3769
4	100	5125
5	100	6486
6	100	7840

Conditions: $T = 110^\circ\text{C}$, $p = 10$ bar H_2 , 500 ppm Rh, $t = 30$ min, stirring velocity = 1000 rpm.

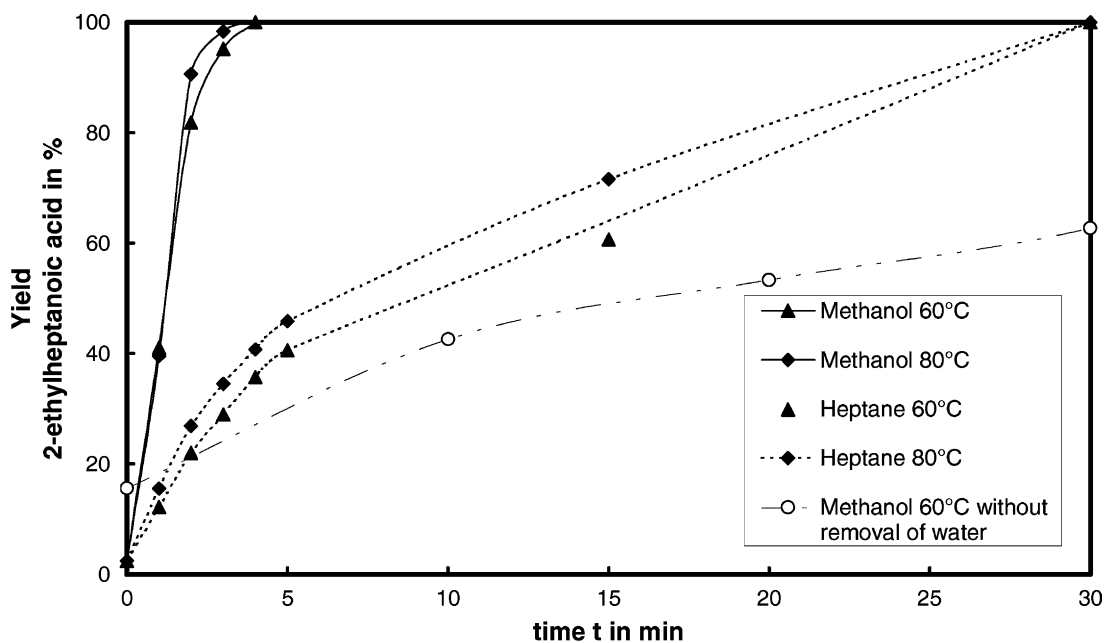
ture of the aliphatic carboxylic acids. Although the desired product, 2-ethylheptanoic acid (**2**), is already obtained in small amounts by homogeneous biphasic hydrogenation, a quantitative yield is only achieved applying a second heterogeneous hydrogenation step.

Heterogeneous hydrogenation catalysts show higher activities in double bond hydrogenation compared to the homogeneous two-phase system. For this reason the cleavage of the δ -lactone ring is done homogeneously in a two-phase system. In the following double bond hydrogenation, a commercial available heterogeneous palladium/charcoal catalyst was applied. This catalyst is very active due to its high surface area and in addition resistant to carboxylic acids.

3.3.1. Investigation of the heterogeneous hydrogenation in different solvents

The heterogeneous hydrogenation was investigated in methanol and *n*-heptane. Methanol is a well-known solvent for hydrogenations; *n*-heptane was chosen because of its complete miscibility gap with water. It could therefore be used as solvent in the two-phase hydrogenation. The results are shown in Fig. 5.

Quantitative yields of 2-ethylheptanoic acids are achieved in the case of methanol after 3–5 min, in the case of *n*-heptane as solvent after 30 min. The reaction rates of the hydrogenations in methanol compared to *n*-heptane are obviously much faster. One reason can be seen in the higher solubility of the



(Conditions: $p(\text{H}_2) = 10$ bar, stirrer velocity = 700 rpm, $m(\text{ethylheptanoic acids}) = 10$ g, $m(\text{Pd/C}) = 0,25\text{g}$)

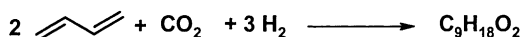
Fig. 5. Comparison of the heterogeneous hydrogenation of the isomeric 2-ethylidene-heptenoic acids in different solvents.

ethylidene-heptenoic acids in methanol. Before the hydrogenations, the reaction mixtures were distilled to remove traces of water which are solved in the organic phase due to the previous two-phase reaction. In contrast to the water free hydrogenations, the presence of only 1% of water in the reaction mixture diminishes the reaction rate considerably showing the inhibition of the catalyst by the water content.

4. Conclusion and outlook

A new three-step process for the convenient production of 2-ethylheptanoic acid (**2**) from the cheap steamcracker product butadiene and the waste gas carbon dioxide has been described [16]. The overall reaction is shown in Scheme 8.

This process consists of the well-known formation of the δ -lactone (**1**). In the second step, a catalytic biphasic hydrogenation of the δ -lactone with



Scheme 8. Overall reaction for the production of 2-ethylheptanoic acid.

water-soluble rhodium catalysts is applied. A catalytic cycle has been proposed, explaining the observed products. The catalyst has been recycled five times without considerable loss of activity. The leaching of the catalyst has found to be in the range of 1 wt.% of the initial catalyst concentration. By an additional extraction unit this loss of catalyst should be avoided. In the third reaction step, the remaining double bonds are hydrogenated using commercially available heterogeneous palladium catalysts. In future works the existing miniplant [8] for the production of the δ -lactone (**1**) could be upgraded to the production of 2-ethylheptanoic acid (**2**).

Compared to the industrial production of the homologous 2-ethyl-hexanoic-acid, the advantages of the new process are the incorporation of carbon dioxide, the few number of reaction steps and the atomic efficiency of the whole process.

Acknowledgements

We would like to thank Dr. B. Costisella for NMR analysis and Mr. W. Elling for ICP measurements.

We are very grateful to Degussa AG for the supply of catalysts and Celanese AG for the supply of TPPTS-solution.

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