

**Process for Pd-catalyzed hydroxycarbonylation of diisobutene:
ratio of 3,5,5-trimethylhexanoic acid/H₂O**

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The invention relates to a process for Pd-catalyzed hydroxycarbonylation of diisobutene:
ratio of 3,5,5-trimethylhexanoic acid/H₂O

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Carboxylic acids including propionic acid, adipic acid and fatty acids are used in the preparation of polymers, pharmaceuticals, solvents and food additives. The routes leading to carboxylic acids generally include the oxidation of hydrocarbons, alcohols or aldehydes, the oxidative cleavage of olefins by ozonolysis, the hydrolysis of triglycerides, nitriles, esters or amides, the carboxylation of Grignard or organolithium reagents, and the halogenation and subsequent hydrolysis of methyl ketones in the haloform reaction.

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The hydroxycarboxylation of olefins is a highly promising and environmentally-friendly method for obtaining carboxylic acids. Acetic acid is produced by carbonylation of methanol, which is carried out with iodide. In the Koch reaction, the addition of water and carbon monoxide to alkenes is catalyzed by strong bases. This method is effective with alkenes that form secondary and tertiary carbocations, e.g. isobutylene to pivalic acid. Hydroxycarboxylation occurring with the simultaneous addition of CO and H₂O to alkenes/alkynes provides a direct and convenient method for synthesizing carboxylic acids.

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The object of the invention was to provide a process affording good conversion in the Pd-catalyzed hydroxycarbonylation of diisobutene (DIBN).

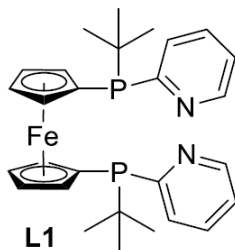
The object is achieved by a process according to Claim 1.

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Process comprising the process steps of:

- a) addition of diisobutene,
- b) addition of a compound comprising Pd, wherein the Pd is capable of forming a complex,

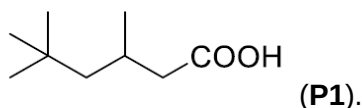
c) addition of the ligand **L1**:



d) addition of 3,5,5-trimethylhexanoic acid and water, wherein the ratio based on the
5 volumes used is in the range from 0.75/1.25 to 1.8/0.2,

e) feeding in CO,

f) heating the reaction mixture such that the diisobutene is converted to the compound **P1**:



10 In one variant of the process, the compound in process step b) is selected from: PdCl₂, PdBr₂, Pd(acac)₂, Pd(dba)₂ (dba = dibenzylideneacetone), PdCl₂(CH₃CN)₂.

In one variant of the process, the compound in process step b) is Pd(acac)₂.

15 In one variant of the process, the process comprises the additional reaction step g):
g) addition of CF₃SO₃H.

In one variant of the process, the reaction mixture is heated to a temperature in the range from 80°C to 160°C in process step f),

20 preferably to a temperature in the range from 100°C to 140°C.

In one variant of the process, the CO is fed in in process step e) such that the reaction proceeds under a CO pressure in the range from 20 bar to 60 bar, preferably in the range from 30 bar to 50 bar.

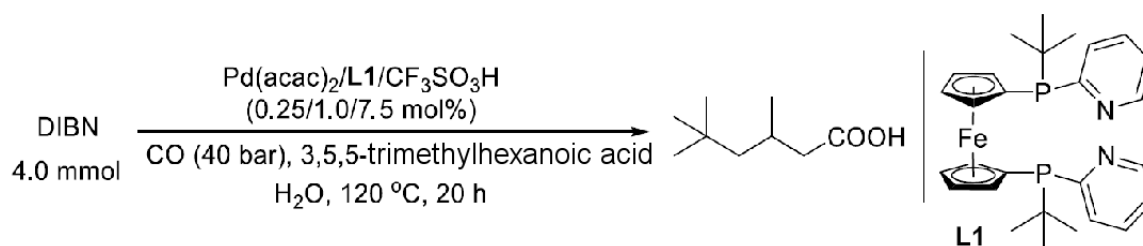
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In one variant of the process, the ratio of 3,5,5-trimethylhexanoic acid/water based on the volumes used is in the range from 1.0/1.0 to 1.8/0.2.

In one variant of the process, the amount of

3,5,5-trimethylhexanoic acid added per 1 mmol of diisobutene is in the range from 0.3 ml to 0.4 ml.

- 5 The invention is elucidated in more detail by means of working examples below.



- A 4 mL vial was charged with $[\text{Pd}(\text{acac})_2]$ (3.05 mg, 0.25 mol%), L1 (20.64 mg, 1.0 mol%) and oven dried stirring bar. The vial was then sealed with septa (PTFE-coated styrene-butadiene rubber) and a phenol resin cap. The vial was evacuated and refilled with argon three times. H_2O (0.5 ml), 3,5,5-trimethylhexanoic acid (1.5 ml), diisobutene (DIBN) (4.0 mmol) and $\text{CF}_3\text{SO}_3\text{H}$ (7.5 mol%) were added to the vial by syringe. The vial was placed in an alloy plate, which was transferred to an autoclave (300 mL) of the 4560 series from Parr Instruments under argon atmosphere. After flushing the autoclave three times with CO, the pressure of CO was increased to 40 bar at room temperature. The reaction was conducted at 120°C for 20 h. On conclusion of the reaction, the autoclave was cooled down to room temperature and cautiously decompressed. Isooctane (100 μl) was then added as internal standard. Conversion was measured by GC analysis.

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The experiment described above was repeated with variation of the ratio of 3,5,5-trimethylhexanoic acid/water. All other parameters were maintained.

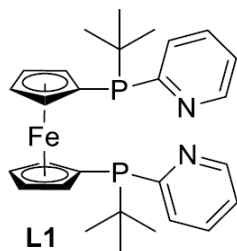
The results are compiled in the following table.

Entry	3,5,5-Trimethylhexanoic acid/water (mL/mL)	Conversion (%)
1	0/2	25
2	0.2/1.8	45
3	0.5/1.5	49
4	1.0/1.0	84
5	1.5/0.5	87
6	1.8/0.2	72

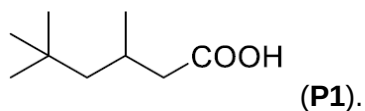
Claims

1. Process comprising the process steps of:

- 5 a) addition of diisobutene,
b) addition of a compound comprising Pd, wherein the Pd is capable of forming a complex,
c) addition of the ligand **L1**:



- 10 d) addition of 3,5,5-trimethylhexanoic acid and water, wherein the ratio based on the volumes used is in the range from 0.75/1.25 to 1.8/0.2,
e) feeding in CO,
f) heating the reaction mixture such that the diisobutene is converted to the compound **P1**:



- 15 2. Process according to Claim 1,
wherein the compound in process step b) is selected from:
 PdCl_2 , PdBr_2 , $\text{Pd}(\text{acac})_2$, $\text{Pd}(\text{dba})_2$ (dba = dibenzylideneacetone), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$.
- 20 3. Process according to either of Claims 1 and 2,
wherein the process comprises the additional reaction step g):
g) addition of $\text{CF}_3\text{SO}_3\text{H}$.
- 25 4. Process according to any of Claims 1 to 3,
wherein the reaction mixture is heated to a temperature in the range from 80°C to 160°C in process step f).
- 30 5. Process according to any of Claims 1 to 4,
wherein the CO is fed in in process step e) such that the reaction proceeds under a CO pressure in the range from 20 bar to 60 bar.

6. Process according to any of Claims 1 to 5,
wherein the ratio of 3,5,5-trimethylhexanoic acid/water based on the volumes used
is in the range from 1.0/1.0 to 1.8/0.2.

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7. Process according to any of Claims 1 to 6,
wherein the amount of 3,5,5-trimethylhexanoic acid added per 1 mmol of
diisobutene is in the range from 0.3 ml to 0.4 ml.