

Process for Pd-catalyzed hydroxycarbonylation of diisobutene:**Sulfuric acid/ligand ratio**

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The invention relates to a process for Pd-catalyzed hydroxycarbonylation of diisobutene: sulfuric acid/ligand ratio.

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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 hydrocarboxylation 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. The hydrocarboxylation 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). This reaction should be carried out in one step.

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

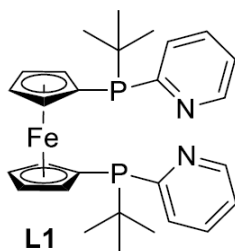
Process comprising the process steps of:

a) addition of diisobutene,

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

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

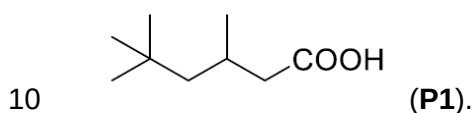


d) addition of acetic acid,

5 e) addition of sulfuric acid, wherein the sulfuric acid is added in an amount which is at least 3.5 mol of sulfuric acid per mole of ligand **L1**,

f) feeding in CO,

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



In one variant of the process, 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), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$.

15 In one variant of the process, the compound in process step b) is $\text{Pd}(\text{acac})_2$.

In one variant of the process, the sulfuric acid is added in an amount which is in the range from 3.5 mol to 5 mol of sulfuric acid per mole of ligand **L1**.

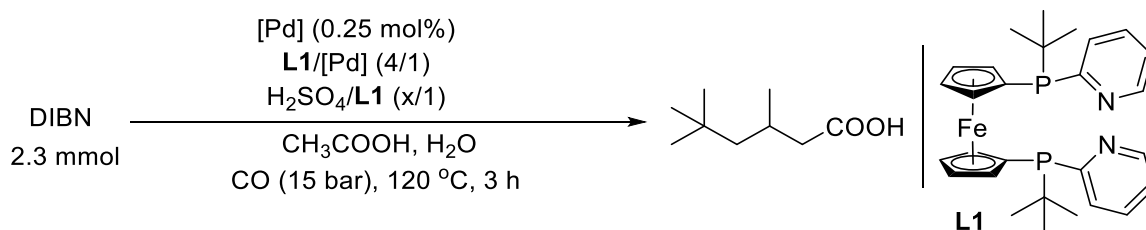
20 In one variant of the process, the sulfuric acid is added in an amount which is in the range from 3.5 mol to 4.5 mol of sulfuric acid per mole of ligand **L1**.

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 g), preferably to a temperature in the range from

25 100°C to 140°C.

In one variant of the process, the CO is fed in in process step f) such that the reaction proceeds under a CO pressure in the range from 10 bar to 40 bar, preferably in the range from 10 bar to 30 bar.

The invention is more particularly elucidated hereinbelow with reference to working examples.



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A 4 ml vial was charged with $[\text{Pd}(\text{acac})_2]$ (1.75 mg, 0.25 mol%), L1 (11.83 mg, 1.0 mol%), H_2SO_4 (3.1 mg, 1.4 mol%) and a stirrer bar that had been dried in an oven. 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 (0.29 ml), acetic acid
 10 (0.85 ml) and diisobutene (DIBN) (2.3 mmol) were added to the vial with a 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 CO pressure was increased to 15 bar at room temperature, and subsequently increased to a pressure of 25 bar with N_2 . The reaction was conducted at
 15 120°C for 3 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.

The above-described experiment was repeated while varying the $\text{H}_2\text{SO}_4/\text{L1}$ ratio. All other
 20 parameters were maintained.

The results are compiled in the following table.

Entry	$\text{H}_2\text{SO}_4/\text{L1}$ (mmol/mmol) - H_2SO_4 (x mol%)	Conversion (%)
1	1.4/1 - 1.4	69
2	3.0/1 - 3.0	83
3*	3.75/1 - 3.75	90
4*	4.0/1 - 4.0	92

* inventive process

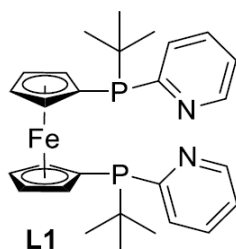
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As the experimental results show, the object is achieved by the inventive process.

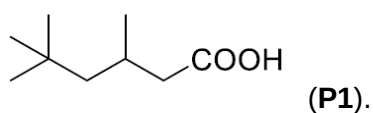
Claims

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 acetic acid,
e) addition of sulfuric acid, wherein the sulfuric acid is added in an amount which is at least 3.5 mol of sulfuric acid per mole of ligand **L1**,
f) feeding in CO,
g) 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 any of Claims 1 to 2,
wherein the sulfuric acid is added in an amount which is in the range from 3.5 mol to 5 mol of sulfuric acid per mole of ligand **L1**.
- 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 g).

5. Process according to any of Claims 1 to 4,
wherein the CO is fed in in process step f) such that the reaction proceeds under a
CO pressure in the range from 10 bar to 40 bar.