

Process for Pd-catalyzed hydroxycarbonylation of diisobutene:**Effect of solvent**

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The invention relates to a process for Pd-catalyzed hydroxycarbonylation of diisobutene:
Effect of solvent

10 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
20 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.

25 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.

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

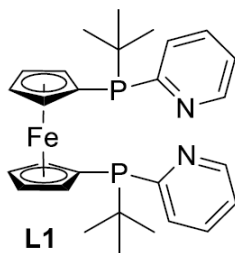
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Process comprising the process steps of:

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

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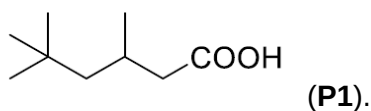
c) addition of the ligand **L1**:



d) addition of acetic acid,

e) feeding in CO,

5 f) 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: PdCl₂, PdBr₂, Pd(acac)₂, Pd(dba)₂ (dba = dibenzylideneacetone), PdCl₂(CH₃CN)₂.

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

In one variant of the process, the process comprises the additional reaction step g):

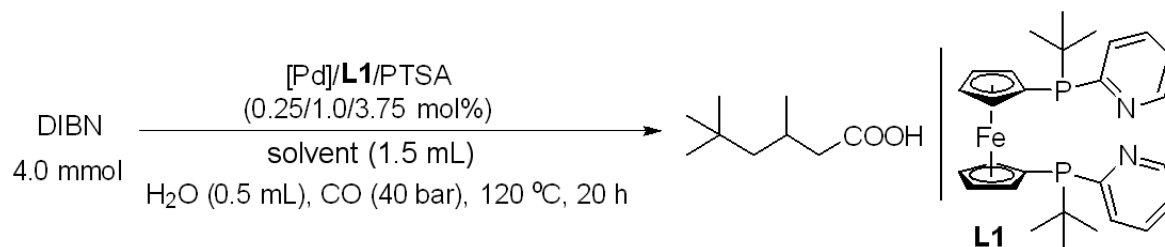
15 g) addition of p-toluenesulfonic acid (PTSA).

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

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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.

The invention is elucidated in more detail by means of a working example below.



A 4 ml vial was charged with [Pd(acac)₂] (3.05 mg, 0.25 mol%), L1 (20.64 mg, 1.0 mol%),
 5 PTSA*H₂O (28.5 mg, 3.75 mol%) and an oven-dried stirrer 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. H₂O (0.5 ml), acetic acid (1.5 ml) and
 diisobutene (DIBN) (4.0 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
 10 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 solvent. All other parameters were maintained.

The results are compiled in the following table.

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Entry	Solvent	Conversion (%)
1	3,5,5-trimethylhexanoic acid	88
2	Formic acid	48
3*	Acetic acid	>99

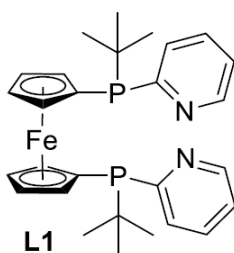
* inventive process

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

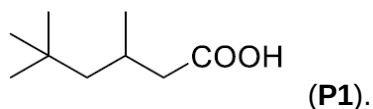
Claims

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) 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 p-toluenesulfonic acid.
- 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).
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.