

Process for the preparation of dicidal

The present invention relates to a process for the preparation of dicidal.

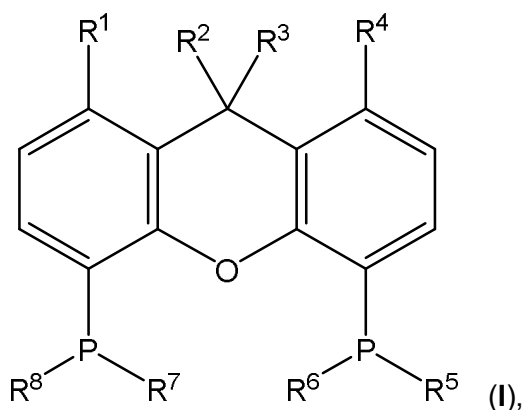
- 5 US 2009/0171125 A1 describes a process for the hydroformylation of cyclic olefins. In this case an Rh catalyst is used.

The present invention has the object of providing a novel hydroformylation process. The process should afford an increased yield in comparison to the method known from the
10 prior art.

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

Process comprising the process steps of:

- 15 a) initially charging dicyclopentadiene;
b) adding a compound of formula (I):



where R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 are selected from: -H, $-(C_1-C_{12})$ -alkyl, -Ph;

- c) adding a Pt compound capable of forming a complex;
20 d) adding an iodine compound;
e) feeding in CO and H_2 ;
f) heating the reaction mixture from steps a) to e), to convert the dicyclopentadiene to dicidal.
- 25 In this process, process steps a) to e) can be effected in any desired sequence. Typically, however, CO and H_2 are added after the co-reactants have been initially charged in steps a) to d).

Here, process steps c) and d) may also be carried out in one step, for example by adding PtI_2 .

In one variant of the process, the Pt compound and the iodine compound are added in one step by adding PtI_2 .

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The expression $(\text{C}_1\text{-C}_{12})$ -alkyl encompasses straight-chain and branched alkyl groups having 1 to 12 carbon atoms. These are preferably $(\text{C}_1\text{-C}_8)$ -alkyl groups, more preferably $(\text{C}_1\text{-C}_6)$ -alkyl, most preferably $(\text{C}_1\text{-C}_4)$ -alkyl.

- 10 Suitable $(\text{C}_1\text{-C}_{12})$ -alkyl groups are especially methyl, ethyl, propyl, isopropyl, *n*-butyl, *isobutyl*, *sec*-butyl, *tert*-butyl, *n*-pentyl, 2-pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, *n*-hexyl, 2-hexyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 2,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-
- 15 trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl, 1-ethyl-2-methylpropyl, *n*-heptyl, 2-heptyl, 3-heptyl, 2-ethylpentyl, 1-propylbutyl, *n*-octyl, 2-ethylhexyl, 2-propylheptyl, nonyl, decyl.

In one variant of the process, R^1 and R^4 are -H.

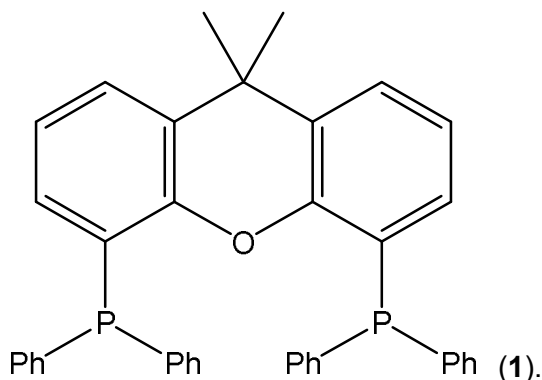
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In one variant of the process, R^5 , R^6 , R^7 , R^8 are -Ph.

In one variant of the process, R^2 and R^3 are $(\text{C}_1\text{-C}_{12})$ -alkyl.

- 25 In one variant of the process, R^2 and R^3 are $-\text{CH}_3$.

In one variant of the process, the compound (I) has the structure (1):



In one variant of the process, the Pt compound is selected from: Pt(II)I₂, Pt(IV)I₄, diphenyl(1,5-COD)Pt(II), Pt(II)(acac)₂, Pt(0)(PPh₃)₄, Pt(0)(DVTs) solution (CAS:68478-92-2), Pt(0)(ethylene)(PPh₃)₂, tris(benzylideneacetone)Pt(0), Pt(II)(OAc)₂ solution, Pt(0)(t-Bu)₂, Pt(II)(COD)Me₂, Pt(II)(COD)I₂, Pt(IV)I Me₃, Pt(II)(hexafluoroacetylacetonate)₂.

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In one variant of the process, the Pt compound is selected from: Pt(II)I₂, Pt(II)(acac)₂.

In one variant of the process, the Pt compound is Pt(II)I₂.

- 10 In one variant of the process, the iodine compound is selected from: alkali metal halide, alkaline earth metal halide, NH₄X, alkylammonium halide, dialkyl halide, trialkyl halide, tetraalkyl halide, cycloalkylammonium halide.

In one variant of the process, the iodine compound is selected from: Pt(II)I₂, LiI.

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In one variant of the process, PtI₂ is added in an amount, measured in mol% based on dicyclopentadiene, such that the value is in the range from 0.1 mol% to 5 mol%.

- 20 In one variant of the process, PtI₂ is added in an amount, measured in mol% based on dicyclopentadiene, such that the value is in the range from 0.1 mol% to 3 mol%.

In one variant of the process, PtI₂ is added in an amount, measured in mol% based on dicyclopentadiene, such that the value is in the range from 0.1 mol% to 1 mol%.

- 25 In one variant of the process, this process comprises the additional process step e'): e') adding a solvent.

- 30 In one variant of the process, the solvent is selected from: THF, DCM, ACN, heptane, DMF, toluene, texanol, pentane, hexane, octane, isooctane, decane, dodecane, cyclohexane, benzene, xylene, marlotherm, propylene carbonate, MTBE, diglyme, triglyme, diethyl ether, dioxane, isopropanol, tert-butanol, isononanol, isobutanol, isopentanol, ethyl acetate.

- 35 In one variant of the process, the solvent is selected from: THF, DCM, ACN, heptane, DMF, toluene, texanol.

In one variant of the process, CO and H₂ is fed in at a pressure in a range from 1 MPa (10 bar) to 6 MPa (60 bar).

In one variant of the process, CO and H₂ is fed in at a pressure in a range from 2 MPa (20 bar) to 5 MPa (50 bar).

In one variant of the process, the reaction mixture is heated to a temperature in the range from 25°C to 150°C.

In one variant of the process, the reaction mixture is heated to a temperature in the range from 30°C to 130°C.

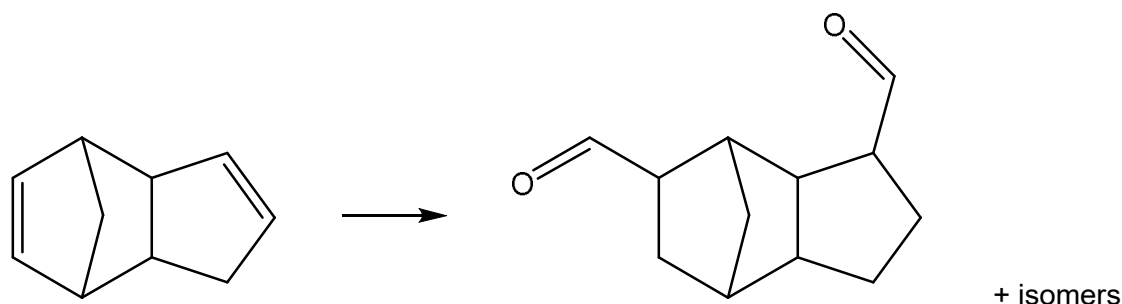
In one variant of the process, the process comprises the additional process step g):
g) converting dicidal to didicol.

In one variant of the process, the conversion of dicidal to didicol is carried out using “Shvo’s catalyst” (CAS 104439-77-2).

The invention is to be illustrated in detail hereinafter by a working example.

Experimental description

Conversion of dicyclopentadiene to dicidal



10 mmol of dicyclopentadiene (DCPD), 10 ml of absolute toluene, 0.5 mol% PtI₂, 2.2 equivalents of xantphos (**1**) (based on Pt) are placed under argon in a 25 ml steel autoclave from Parr Instruments. The autoclave was pressurized to 40 bar with synthesis gas (CO/H₂ = 1:1) and the reaction started by heating to 80°C and stirring. This reaction is

In a comparative example, Rh(acac)(CO)₂ was added instead of PtI₂.

Ptl₂: 89.5%

Rh(acac)(CO)₂: < 5%

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10 ml of toluene, 5 ml of ethanol, 5.5 g of dicidal (28.6 mmol) and 62.16 mg of “Shvo’s catalyst” (CAS 104439-77-2) (0.2 mol% with respect to dicidal) are heated to 100°C under argon in a 100 ml Parr pressure autoclave at 40 bar hydrogen and reacted while stirring for 20 hours. The reaction is then stopped, the pressure released and the reaction mixture distilled in a fine vacuum. A colourless oil of the isomeric mixture of didicol is obtained as a fraction at 140°C.

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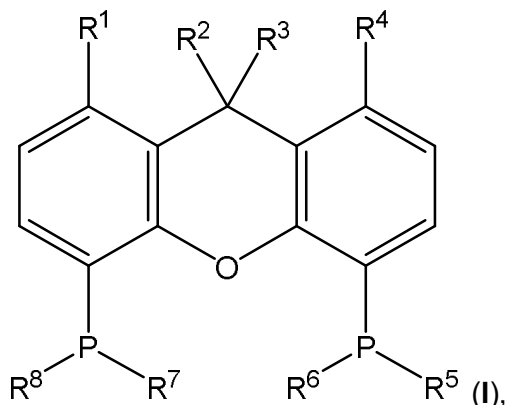
As the experimental results show, the object is achieved by the inventive process.

Claims

1. Process comprising the process steps of:

a) initially charging dicyclopentadiene;

5 b) adding a compound of formula (I):



where $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8$ are selected from: -H, $-(C_1-C_{12})$ -alkyl, -Ph;

c) adding a Pt compound capable of forming a complex;

d) adding an iodine compound;

10 e) feeding in CO and H_2 ;

f) heating the reaction mixture from steps a) to e), to convert the dicyclopentadiene to dicidal.

2. Process according to Claim 1,

15 where R^1 and R^4 are -H.

3. Process according to either of Claims 1 and 2,

where R^5, R^6, R^7, R^8 are -Ph.

20 4. Process according to any of Claims 1 to 3,

where R^2 and R^3 are $-(C_1-C_{12})$ -alkyl.

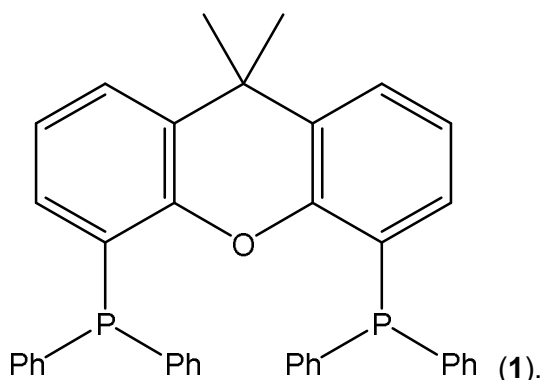
5. Process according to any of Claims 1 to 4,

where R^2 and R^3 are $-CH_3$.

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6. Process according to any of Claims 1 to 5,

wherein the compound (I) has the structure (1):



7. Process according to any of Claims 1 to 6,
 wherein the Pt compound is selected from: Pt(II)I₂, Pt(IV)I₄, diphenyl(1,5-COD)Pt(II),
 5 Pt(II)(acac)₂, Pt(0)(PPh₃)₄, Pt(0)(DVTs) solution (CAS:68478-92-2),
 Pt(0)(ethylene)(PPh₃)₂, tris(benzylideneacetone)Pt(0), Pt(II)(OAc)₂ solution, Pt(0)(t-Bu)₂,
 Pt(II)(COD)Me₂, Pt(II)(COD)I₂, Pt(IV)I Me₃, Pt(II)(hexafluoroacetylacetonate)₂.
8. Process according to any of Claims 1 to 7,
 10 wherein the iodine compound is selected from: Pt(II)I₂, LiI.
9. Process according to any of Claims 1 to 8,
 wherein PtI₂ is added in an amount, measured in mol% based on dicyclopentadiene, such
 that the value is in the range from 0.1 mol% to 5 mol%.
- 15 10. Process according to any of Claims 1 to 9,
 comprising the additional process step e'):
 e') adding a solvent.
- 20 11. Process according to any of Claims 1 to 10,
 wherein CO and H₂ is fed in at a pressure in a range from 1 MPa (10 bar) to 6 MPa (60
 bar).
12. Process according to any of Claims 1 to 11,
 25 wherein the reaction mixture is heated to a temperature in the range from 25°C to 150°C.
13. Process according to any of Claims 1 to 12,
 wherein the process comprises the additional process step g):
 g) converting dicidal to dicidol.

14. Process according to Claim 13,
wherein the conversion of dicidal to dicidol is carried out using "Shvo's catalyst" (CAS
104439-77-2).