

METHOD FOR PREPARING CARBOXYLIC ACIDS BY PALLADIUM CARBONYLATION

The present invention relates to a process  
5 for the preparation of  $\beta$ - or  $\gamma$ -unsaturated or saturated  
carboxylic acids.

It relates more particularly to the  
hydroxycarbonylation of an organic compound comprising  
a conjugated unsaturation, such as butadiene, by the  
10 action of carbon monoxide and water in the presence of  
a palladium-based catalyst. The carboxylic acids thus  
obtained are preferably pentenoic acids.

One of the possible routes of access to  
adipic acid, which is one of the two basic constituents  
15 of polyamides, such as polyamide 6,6, is the double  
carbonylation of butadiene or its derivatives.

Although it is possible to imagine carrying  
out the two hydroxycarbonylations leading from  
butadiene to adipic acid in a single stage, it turns  
20 out in practice that the two reactions have to be  
carried out successively if it is desired to obtain  
selectivities which are sufficiently high to be able to  
envisage an economically viable industrial process.

Patent US-A-3 509 209 discloses the  
25 hydroxycarbonylation of various olefins, including

butadiene, by carbon monoxide and water in the presence of hydrochloric acid or hydrobromic acid and of a palladium-comprising catalyst at a temperature of 15°C to 300°C and under a pressure of 1 to 1 000 bar, preferably of 10 to 200 bar.

Under the conditions described, it is observed that the yields of pentenoic acids are very low and that, in reality, the product obtained is very often valerolactone.

Patent FR-A-2 529 885 has provided a process for the preparation of  $\beta$ - or  $\gamma$ -unsaturated acids, such as pentenoic acids, by carbonylation of a conjugated diene (more particularly butadiene) in the presence of water, of a hydrohalic acid, of a palladium-based catalyst and of a quaternary onium salt, the onium being that of an element chosen from nitrogen, phosphorus and arsenic.

This process gives good results but it requires the use of a relatively large amount of a quaternary onium salt, which is an expensive compound and one whose presence is of such a nature as to complicate the treatment of the mixtures at the end of the reaction.

European Patent 0 648 731 also discloses a process for the hydroxycarbonylation of butadiene and its derivatives to pentenoic acids in the presence of

crotyl chloride, in the proportion of at least two mol per mole of palladium, the palladium being at least partially in the form of a  $\pi$ -crotyl complex. This process makes it possible to avoid the use of onium  
5 salt.

These various processes make possible the manufacture of carboxylic acids with acceptable yields and selectivities. However, the recovery and the recycling of the catalyst has never been described in  
10 these documents. As the metal used is a precious metal, the partial recovery of this catalyst does not allow an industrial development of these processes.

One of the aims of the present invention is to provide a hydroxycarbonylation process comprising a  
15 complete or substantially complete recovery of the palladium catalyst. Furthermore, the invention provides a recovery of the palladium which makes possible recycling of the latter in a further hydroxycarbonylation stage.

20 To this end, the invention provides a process for the manufacture of  $\beta$ - or  $\gamma$ -unsaturated carboxylic acids or of saturated carboxylic acids by reaction, with carbon monoxide and water, of a compound comprising an ethylenic or acetylenic unsaturation  
25 conjugated with another unsaturation or an electron-

donating group carried by the carbon in the position  $\alpha$  to the said unsaturation. This reaction is carried out in the presence of a palladium-based catalyst which is soluble in the medium.

In an aspect of the present invention, there is provided a process for the preparation of unsaturated or saturated carboxylic acids [sic] from compounds comprising an ethylenic or acetylenic unsaturation conjugated with another unsaturation or an electron-donating group by reaction of carbon monoxide and water in the presence of a palladium-based catalyst, characterized in that it consists in treating the reaction medium, after the end of the hydroxycarbonylation reaction, by extraction of the carbon monoxide from the said reaction medium by treatment with a gas, in order to obtain a CO concentration of less than 600 ml of CO per litre of solution, then treatment of [sic] the reaction medium with hydrogen to reduce the palladium to the zero oxidation state and in separating the precipitated palladium from the reaction medium.

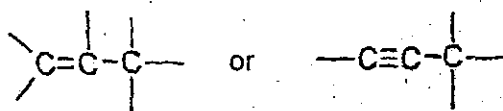
The process of the invention is characterized in that the reaction medium, at the end of the hydroxycarbonylation reaction, is treated in a first stage, in order to extract the carbon monoxide present in the medium by evaporation or entrainment of the CO, and then in a second stage, in order to reduce the palladium present in the medium to palladium in the zero oxidation state by treatment with hydrogen. The palladium thus reduced precipitates and can be

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separated from the reaction medium by conventional  
15 solid/liquid separating means.

According to one characteristic of the  
invention, the concentration of CO in the medium before  
treatment with hydrogen is advantageously less than  
600 ml of CO per litre of solution, preferably less  
20 than 100 ml of CO per litre of solution. The  
concentration of CO is also preferably greater than  
0.001 ml of CO per litre of solution.

The term "compounds comprising an  
unsaturation" should be understood as meaning the  
25 compounds of general formulae:



in which the carbon in the  $\alpha$  position with respect to the ethylenic or acetylenic unsaturation also carries  
5 an ethylenic unsaturation or an electron-donating radical, such as, for example, halogen atoms, substituted or unsubstituted amino groups, or alkoxy, hydroxyl, oxo, epoxy, carbonyl, mercaptoalkyl, ester and/or cyano groups.

10           Mention may be made, as examples of such unsaturated compounds, of diolefins, allyl alcohols, allyl ethers, allyl esters and allyl halides.

The preferred compound of the invention is butadiene, which makes possible the manufacture of  
15 pentenoic acids by simple hydroxycarbonylation or adipic acid by double hydroxycarbonylation.

The catalyst of the invention is a palladium compound which is soluble in the reaction medium. The compounds for the implementation of the invention are  
20 those described in the documents cited above to illustrate the state of the art.

Mention may be made, for example, of palladium compounds comprising one or more anionic groups, such as, for example, those derived from

hydrochloric, hydriodic, hydrofluoric or hydrobromic acids, sulphuric acid, nitric acid or carbonic acid.

Anionic groups derived from sulphonic acids, thioalcohols or carboxylic acids, such as acetic acid, propionic acid or pivalic acid, or the like, are also suitable.

Use may also be made of complexes formed from compounds comprising phosphorus or nitrogen atoms.

The palladium can also be present in the form of organic complexes, which can be formed before the introduction into the reaction medium or directly in the said medium.

Examples of complexes which can be used in the present process are:

bis( $\pi$ -allylpalladium chloride), bis( $\pi$ -allylpalladium bromide), acetylacetonato(allyl)palladium, bis( $\pi$ -isobutenylpalladium chloride), bis( $\pi$ -cyclohexenylpalladium chloride) and other  $\pi$ -allyl complexes, such as bis( $\pi$ -4-chlorocrotylpalladium chloride) and bis( $\pi$ -2-methyl-4-chlorocrotylpalladium chloride),  $\pi$ -allylcarbonylpalladium chlorides and  $\pi$ -isobutenylcarbonylpalladium chloride, respectively, for example  $(C_4H_7Pd_2Cl_2CO)_2$  [sic], and, furthermore, ethylenepalladium chloride.

It is also possible to use organic palladium

complexes, such as palladium acetylacetonate,  
bis(bibenzylideneacetone)palladium, the dimer of  
palladium crotyl chloride, or complexes of aromatic or  
aliphatic phosphines with palladium, such as  
5 tetrakis(triphenylphosphine)palladium or  
bis(triphenylphosphine)palladium dichloride.

According to a preferred embodiment of the  
invention, the palladium catalyst is formed in situ by  
addition of crotyl chloride, in a proportion of at  
10 least two mol per mole of palladium. The palladium is  
thus at least partially in the form of a  $\pi$ -crotyl  
complex, as disclosed in European Patent No. 0 648 731.

According to the invention, the process for  
the hydroxycarbonylation of unsaturated organic  
15 compounds described above, which compounds will be  
exemplified for more clarity with reference to  
butadiene, by carbon monoxide and water is  
advantageously carried out at a carbon monoxide  
pressure greater than atmospheric pressure.

20 Advantageously, the water present in the  
reaction medium represents an amount of less than or  
equal to 20% by weight with respect to the weight of  
the reaction mixture.

The term "butadiene derivative" is understood  
25 to mean, in the present text, in particular allylic  
butenols, such as 3-butene-2-ol [sic], 2-butene-1-ol

[sic] and their mixtures, or addition compounds of hydrogen chloride with butadiene (chlorobutenes), the main one of which is crotyl chloride.

In the present process, it is possible to  
5 employ butadiene, one or more of its derivatives or mixtures of butadiene with one or more of its derivatives. Butadiene or mixtures predominantly comprising butadiene represent, however, the preferred substrates.

10 The  $\pi$ -crotylpalladium complex catalyst can be introduced into the reaction medium or can be formed in situ from Pd halides, more particularly the chloride, [lacuna] Pd carboxylates, in particular the acetate, or from finely divided palladium metal.

15 The amount of  $\pi$ -crotylpalladium catalyst used in the process can vary within wide limits. Generally, from  $10^{-5}$  mol to 0.2 mol of Pd is employed per mole of butadiene or of butadiene derivative charged to the reaction and preferably from  $10^{-4}$  mol to 0.1 mol per  
20 mole.

In addition to the  $\pi$ -crotylpalladium catalyst, palladium can also be found in the reaction medium in another less active form (for example, Pd metal or Pd chloride) in a variable amount. In an  
25 industrial process, it is, however, preferable for all

or virtually all the palladium to be in an active form which is soluble in the medium, such as  $\pi$ -crotylpalladium, optionally with palladium chloride.

The  $\pi$ -crotylpalladium complex can be prepared, for example, by reacting a palladium salt, such as palladium chloride, with crotyl chloride in a solvent which can be composed of a water/methanol mixture. The mixture is stirred, generally at ambient temperature, advantageously under a gentle stream of carbon monoxide. The  $\pi$ -crotylpalladium complex precipitates. After an optional degassing phase, the mixture is poured into water and is then extracted using a suitable organic solvent, such as, for example, chloroform. The complex is subsequently isolated from the organic solution by evaporation of the solvent.

The crotyl chloride promoter may be introduced into the reaction mixture or can be formed in situ from butadiene and/or 2-butene-1-ol [sic] and hydrochloric acid.

It preferably represents, as mole per mole, from 5 to 10 times the amount of palladium, although it can be present in larger proportions, since it can constitute all or part of the substrate to be hydroxycarbonylated.

Taken as a whole, it is preferable to have,

in the reaction medium, a Cl/Pd molar ratio of less than or equal to 100 and preferably of less than or equal to 20, as high ratios have a harmful effect on the kinetics of the reaction.

5           As indicated above, the concentration of water in the reaction mixture is advantageously maintained at a value equal to or less than 20% by weight with respect to the weight of the said mixture. This is because the concentration of water has an  
10 effect on the kinetics of the reaction. This concentration of water will preferably be maintained at a value of equal to or less than 8% by weight and more preferably still at a value of equal to or less than 5%.

15           As water is an essential reactant in the hydroxycarbonylation reaction, an advantageous alternative form of the process of the invention consists in injecting this water as the reaction progresses, which makes it possible to maintain its  
20 concentration in the reaction mixture at a very low value while making it possible for the reaction to be carried out.

          Although the presence of a third solvent is not excluded, the reaction is generally carried out  
25 without a solvent other than the reactants themselves or the reaction products. It can also be favourable to

introduce, from the beginning of the hydroxycarbonylation reaction, a pentenoic acid and more particularly pentene-3-oic [sic] acid, in order to minimize side reactions.

5           In the context of an industrial implementation of the process, operations in which the unreacted butadiene is recycled can lead to the introduction, into the reaction medium, of more or less significant amounts of other compounds, in particular  
10 byproducts formed during the hydroxycarbonylation reaction. Thus, it is possible to have, in the reaction mixture, butenes,  $\gamma$ -valerolactone, valeric acid, adipic acid, 2-methylglutaric acid, 2-ethylsuccinic acid, 2-methylbutanoic acid or 2-methylbutenoic acids, for  
15 example. In view of the requirements of a possible continuous implementation of the process, the amounts of these compounds present can reach up to 90% by weight of the reaction mixture charged to the hydroxycarbonylation reaction.

20           The concentration of butadiene is a significant reaction parameter, in particular as regards the stability of the palladium catalyst, that is to say essentially its maintenance in solution in the reaction mixture. It has thus been observed that it  
25 is unfavourable to have less than 0.2% by weight of butadiene with respect to the total weight of the

reaction mixture. Preferably, when the reaction is carried out batchwise, the conversion of the butadiene or its derivatives will be limited so that the reaction mixture includes at least 0.5% by weight of the said  
5 butadiene or its derivatives.

The concentration of butadiene will also preferably be maintained at a value of less than or equal to 50% as weight by weight of the reaction mixture and more preferably still at a value of equal  
10 to or less than 30%, when the reaction is carried out in a batchwise process, and at a value of equal to or less than 10%, when the reaction is carried out in a continuous process.

The embodiment of the hydroxycarbonylation  
15 process described above exhibits the advantage, with respect to other embodiments, of keeping the palladium in solution in the reaction medium up to the end of the reaction, making it possible to maintain high kinetics.

The hydroxycarbonylation reaction can be  
20 carried out at a temperature generally situated between 60°C and 230°C and preferably between 90°C and 200°C and under a pressure, at the temperature, of 50 to 500 bar and preferably from 100 to 300 bar.

The carbon monoxide partial pressure,  
25 measured at 25°C, is from 25 bar to 440 bar and preferably from 55 bar to 240 bar.

As has been indicated, the process of the invention can be carried out continuously or batchwise. There will therefore be good reason to adjust the various operating conditions defined above according to the implementation chosen.

The reaction medium obtained at the end of the hydroxycarbonylation reaction comprises palladium in the dissolved form.

The invention provides a treatment of this reaction medium which makes it possible to recover palladium in the insoluble form with a degree of recovery of approximately 100%.

This treatment consists, in a first stage, in extracting the carbon monoxide dissolved in the reaction medium. This extraction can be obtained by heating the medium with an atmosphere not comprising CO. More advantageously, this extraction is carried out by placing the reaction medium under an inert or hydrogen atmosphere, optionally with sparging of this inert gas or hydrogen into the reaction medium. The term "inert gas" is understood to mean nitrogen or the rare gases.

This stage can be carried out at a temperature of between 20°C (ambient temperature) and 150°C.

This operation is carried out to extract

virtually all the carbon monoxide which can be extracted from the reaction medium. Thus, the concentration of carbon monoxide in the reaction medium can advantageously be less than 600 ml/l, preferably less than 100 ml/l, of solution. Advantageously, the concentration of CO in the reaction medium is between 0.001 ml/l and 600 ml/l.

After extraction of the carbon monoxide, the process of the invention comprises a stage of reduction of the dissolved palladium, generally in the 2+ oxidation state, to palladium in the zero oxidation state (Pd(0)). This palladium is separated from the reaction medium by the usual liquid/solid separating techniques, such as filtration, separation by settling, centrifugation, distillation or evaporation of the liquid medium.

According to a preferred embodiment of the invention, a compound which is insoluble in the reaction medium is present in the said medium before the precipitation of the Pd(0).

This insoluble compound can be added to the reaction medium at any time, for example at the beginning of the hydroxycarbonylation process, at the end of the latter or immediately before the stage of reduction of the palladium.

This insoluble compound is advantageously

added before the beginning of the hydroxycarbonylation reaction.

According to the invention, the palladium in the zero oxidation state precipitates and is deposited  
5 on or in the heterogeneous phase composed of this insoluble compound, thus facilitating its extraction and its separation from the reaction medium.

Generally, this insoluble compound should not have an effect on the hydroxycarbonylation reaction, in  
10 particular should not influence the catalytic effect of the palladium or the selectivity of the reaction.

Mention may be made, as insoluble compounds which are suitable for the invention, of inorganic compounds which are advantageously porous or which  
15 exhibit a large specific surface area. Mention may be made, in this family of compounds, as examples, of active charcoals, alumina, silica, zirconia, cerium oxide or more generally rare earth metal oxides.

Mention may be made, as other insoluble  
20 compounds which are suitable for the invention, of polymer foams, such as polystyrene foams, or silicone oils.

The amount of insoluble compounds added is not critical and can vary within wide limits.

25 According to one characteristic of the invention, the stage of reduction of the palladium to

the zero oxidation state is carried out by placing the reaction medium under a hydrogen atmosphere.

However, it is also possible, without departing from the scope of the invention, to add a  
5 reducing compound to the medium, such as borohydrides, such as  $\text{NaBH}_4$ , for example, or metal hydrides.

This reducing stage can be carried out between ambient temperature ( $20^\circ\text{C}$ ) and  $150^\circ\text{C}$  and  
[lacuna] a hydrogen pressure of between 1 bar and  
10 100 bar.

However, in an embodiment which makes it possible to reduce the palladium to the zero oxidation state without affecting the unsaturation or  
unsaturations present in the hydrocarbonyl compound,  
15 the temperature of the reducing stage is advantageously between  $20^\circ\text{C}$  (ambient temperature) and  $80^\circ\text{C}$ .

In the other embodiment, with a temperature of between  $80^\circ\text{C}$  and  $150^\circ\text{C}$ , the unsaturations of the carboxylic acid obtained by hydrocarbonylation can be  
20 hydrogenated to obtain a saturated carboxylic acid. The process of the invention thus makes it possible, starting from butadiene, to produce pentanoic acid.

The process of the invention makes it possible to recover all the palladium present in the  
25 reaction medium.

In addition, the insoluble compound

comprising the palladium can be treated with acids to redissolve the palladium and to make it possible to recycle it in a further hydroxycarbonylation stage.

The process of the invention thus makes it possible to implement the reactions for the hydroxycarbonylation of unsaturated compounds with catalysis with palladium without loss of catalyst. Such a process can thus be operated economically.

The invention will be more fully illustrated by the examples given below, which are solely by way of illustration and without limiting effect.

#### Example 1

The following are charged to a glass flask:

|                                   |        |             |
|-----------------------------------|--------|-------------|
| 3-Pentenoic acid (90% purity)     | 10.0 g |             |
| Butadiene                         | 2.7 g  | (50 mmol)   |
| Chlorobutene                      | 0.3 g  | (0.35 mmol) |
| Water                             | 0.9 g  | (50 mmol)   |
| Palladium-on-active-charcoal (3%) | 0.71 g |             |

This Pd/C catalyst is sold by Engelhard under the trade name Escat® 162 5207.

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 140°C.

while shaking. When the preset temperature is reached,  
the CO pressure is raised to 200 bar with connection to  
a source of CO to maintain a constant pressure. The CO  
consumption is estimated with respect to the difference  
5 in pressure measured in the source.

After reacting for 40 minutes, corresponding  
to a degree of conversion (DC) of the butadiene of 63%,  
the autoclave is cooled in a water bath to 20°C and  
then degassed. Three purges with hydrogen are carried  
10 out under a pressure of 20 bar of hydrogen. The CO  
content in the medium is 0.6 ml of CO per litre of  
solution.

A pressure of 20 bar of hydrogen is applied  
and the mixture is heated at 80°C with stirring for  
15 one hour (phase of reduction of the palladium). After  
cooling and degassing, the reaction medium is filtered.  
The charcoal collected is dried before analysis.

The reaction mass collected after filtration  
is analysed by liquid chromatography (HPLC) and gas  
20 chromatography (GC).

The following results were obtained:

CY (3-pentenoic acid) = 92%

CY (diacids) = 4.6%

CY (2-methyl-3-butenic acid) = 2.9%

25 CY (pentanoic acid) = 0.07%

Quantitative determination of the palladium

on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that 98% of the palladium charged to the reaction is recovered on the charcoal and 1% is found in the dissolved form in the reaction medium.

The term "degree of conversion (DC) of the butadiene" should be understood as meaning the ratio, expressed as %, of the number of moles of butadiene which have disappeared to the number of moles of butadiene charged.

The term "CY" should be understood as meaning the selectivity for the product X indicated corresponding to the ratio, expressed as %, of the number of moles of product X formed to the number of theoretical moles of product X calculated for the number of moles of butadiene converted.

#### Example 2

The following are charged to a glass flask:

3-Pentenoic acid (90% 10.0 g

purity)

Butadiene 2.6 g

Chlorobutene 0.15 g

Water 0.9 g

Palladium acetate 0.10 g

Charcoal, Ceca L3S 1.1 g

The charcoal is sold by Ceca.

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 140°C while shaking. When the preset temperature is reached, the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

After reacting for 19 minutes, corresponding to a DC of the butadiene equal to 65%, the autoclave is cooled in a water bath to 20°C and then degassed. Two purges with hydrogen are carried out under 20 bar of hydrogen. The solution obtained comprises 40 ml of CO per litre of solution.

A pressure of 20 bar of hydrogen is applied and the mixture is heated at 40°C with stirring for fifteen minutes. After cooling and degassing, the reaction medium is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

CY (3-pentenoic acid) = 83%

CY (diacids) = 11%

CY (2-methyl-3-butenic acid) = 3.6%

CY (pentanoic acid) = 1.8%

Quantitative determination of the palladium  
on the charcoal collected and in the reaction mass  
5 after filtration is carried out by ICP-OES or ICP-MS.  
The results show that 1% of the palladium charged to  
the reaction is found in the dissolved form in the  
reaction medium, the remainder being recovered on the  
charcoal.

10

Example 3

The following are charged to a glass flask:

|                                  |        |
|----------------------------------|--------|
| 3-Pentenoic acid (90%<br>purity) | 10.0 g |
| Butadiene                        | 3.2 g  |
| Chlorobutene                     | 0.32 g |
| Water                            | 0.9 g  |
| Palladium acetate                | 0.10 g |
| Charcoal, Ceca L3S               | 1.0 g  |

The charcoal is sold by Ceca.

The glass flask is introduced into an 125 ml  
autoclave. The latter is immediately pressurized to  
15 100 bar of CO at ambient temperature. The autoclave is  
placed in an oven and the mixture is heated to 140°C  
with shaking. When the preset temperature is reached,  
the CO pressure is brought to 200 bar and the autoclave  
is placed in communication with a source of CO to

maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

After reacting for 23 minutes, corresponding  
5 to a DC of the butadiene equal to 70%, the autoclave is cooled in a water bath to 20°C. The autoclave is reduced in pressure and placed under a pressure of 60 bar with an H<sub>2</sub>/CO mixture with a 95/5 content by weight. The autoclave is heated at 40°C for 45 minutes.  
10 After cooling and degassing, the reaction mixture is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

15 The following results were obtained:

CY (3-pentenoic acid) = 87%

CY (diacids) = 10%

CY (pentanoic acid) = 0.25%

CY (2-methyl-3-butenic acid) = 3.2%

20 Quantitative determination of the palladium on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that only 34% of the palladium charged to the reaction is recovered on the charcoal and 62% is  
25 found in the dissolved form in the reaction medium.

#### Example 4

The following are charged to a glass flask:

3-Pentenoic acid (90%      10.2 g  
purity)

Butadiene                      2.7 g

Chlorobutene                  0.20 g

Water                          0.9 g

Palladium-on-active-  
charcoal (3%)                  1.0 g

This Pd/C catalyst is sold by Engelhard under  
the trade name Escat® 162 5207

The glass flask is introduced into a 125 ml  
5 autoclave. The latter is immediately pressurized to  
100 bar of CO at ambient temperature. The autoclave is  
placed in an oven and the mixture is heated to 140°C  
with shaking. When the preset temperature is reached,  
the CO pressure is brought to 200 bar and the autoclave  
10 is placed in communication with a source of CO to  
maintain a constant pressure. The CO consumption is  
estimated with respect to the difference in pressure  
measured in the source.

After reacting for 24 minutes, corresponding  
15 to a DC of the butadiene equal to 51%, the autoclave is  
cooled in a water bath to 20°C and then slowly  
degassed. No purging is carried out, the CO  
concentration being 1 000 ml of CO per litre of  
solution. A pressure of 20 bar of hydrogen is then

applied and the mixture is heated at 40°C with stirring for fifteen minutes. After cooling and degassing, the reaction medium is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

CY (3-pentenoic acid) = 87%

CY (diacids) = 10%

10 CY (pentanoic acid) = 0.3%

Quantitative determination of the palladium on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that 88% of the palladium charged to the reaction is found in the dissolved form in the reaction medium.

#### Example 5

The following are charged to a glass flask:

|                               |        |
|-------------------------------|--------|
| 3-Pentenoic acid (90% purity) | 10.0 g |
| Butadiene                     | 2.7 g  |
| Chlorobutene                  | 0.30 g |
| Water                         | 0.9 g  |
| Palladium acetate             | 0.11 g |
| Charcoal, Ceca L3S            | 1.0 g  |

The glass flask is introduced into a 125 ml

autoclave. The latter is immediately pressurized to 100 bar of CO at ambient pressure. The autoclave is placed in an oven and the mixture is heated to 140°C with shaking. When the preset temperature is reached, the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

After reacting for 14 minutes, corresponding to a DC of the butadiene equal to 64%, the autoclave is cooled in a water bath to 20°C and then slowly degassed. No purging is carried out. A pressure of 20 bar of hydrogen is then applied and the mixture is heated at 80°C with stirring for fifteen minutes. After cooling and degassing, the reaction medium is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

CY (3-pentenoic acid) = 80%

CY (diacids) = 15%

CY (pentanoic acid) = 0.2%

CY (2-methyl-3-butenic acid) = 3.8%

Quantitative determination of the palladium on the charcoal collected and in the reaction mass

after filtration is carried out by ICP-OES or ICP-MS. The results show that 80% of the palladium charged to the reaction is found in the dissolved form in the reaction medium.

5            Example 6

The following are charged to a glass flask:

|                               |        |
|-------------------------------|--------|
| 3-Pentenoic acid (90% purity) | 10.0 g |
| Butadiene                     | 2.6 g  |
| Chlorobutene                  | 0.30 g |
| Water                         | 0.91 g |
| Palladium acetate             | 0.10 g |
| Charcoal, Ceca L3S            | 1.0 g  |

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient pressure. The autoclave is placed in an oven and the mixture is heated to 140°C with shaking. When the preset temperature is reached, the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

At the end of the reaction, the autoclave is cooled in a water bath to 20°C and then slowly degassed. Purging is carried out with 40 bar of

hydrogen and the CO concentration falls to 40 ml of CO per litre of solution. A pressure of 20 bar of hydrogen is then applied and the mixture is heated at 40°C with stirring for fifteen minutes. After cooling and  
5 degassing, the reaction medium is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

10 CY (3-pentenoic acid) = 80%  
CY (diacids) = 12%  
CY (pentanoic acid) = 2.1%  
CY (2-methyl-3-butenic acid) = 3.9%

Quantitative determination of the palladium  
15 on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that 1% of the palladium charged to the reaction is found in the dissolved form in the reaction medium.

20 Example 7

The following are charged to a glass flask:

|                               |        |
|-------------------------------|--------|
| 3-Pentenoic acid (90% purity) | 10.0 g |
| Butadiene                     | 2.8 g  |
| Chlorobutene                  | 0.31 g |

|                    |        |
|--------------------|--------|
| Water              | 0.9 g  |
| Palladium acetate  | 0.10 g |
| Charcoal, Ceca L3S | 1.0 g  |

The charcoal is sold by Ceca.

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 140°C with shaking. When the preset temperature is reached, the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

At the end of the reaction, the autoclave is cooled in a water bath to 20°C. The autoclave is reduced in pressure, then three purges with hydrogen are carried out under 20 bar of hydrogen (the CO concentration falling to 0.6 ml per litre of solution), then a pressure of 10 bar of hydrogen is applied and the mixture is heated at 80°C with stirring for five minutes. After cooling and degassing, the reaction medium is filtered. The charcoal recovered is dried before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

CY (3-pentenoic acid) = 81%

CY (4-pentenoic acid) = 3.7%

CY (diacids) = 8.5%

5 CY (2-methyl-3-butenic acid) = 3.3%

CY (pentanoic acid) = 4.4%

Quantitative determination of the palladium on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS.

10 The results show that 97% of the palladium charged to the reaction is recovered on the charcoal and 1% is found in the dissolved form in the reaction medium.

#### Example 8

The following are charged to a glass flask:

|                                  |        |
|----------------------------------|--------|
| 3-Pentenoic acid (90%<br>purity) | 10.0 g |
| Butadiene                        | 2.7 g  |
| Chlorobutene                     | 0.30 g |
| Water                            | 0.95 g |
| Palladium acetate                | 0.10 g |
| Alumina, Degussa type C          | 1.0 g  |

15 The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 140°C with shaking. When the preset temperature is reached,

the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

At the end of the test, the autoclave is cooled in a water bath to 20°C and then degassed. Three purges with hydrogen are carried out under 20 bar of hydrogen (the CO concentration falling to 0.6 ml per litre of solution), then a pressure of 20 bar of hydrogen is applied and the mixture is heated at 80°C with stirring for forty-five minutes. After cooling and degassing, the reaction medium is filtered. The alumina recovered is dried before analysis.

Quantitative determination of the palladium on the alumina collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that 97% of the palladium charged to the reaction is recovered on the charcoal [sic] and less than 0.05% is found in the dissolved form in the reaction medium.

#### Example 9

##### 1) Preparation of the $\pi$ -crotyl-Pd chloride complex

5.04 g of PdCl<sub>2</sub>, 3.37 g of NaCl, 50 cm<sup>3</sup> of methanol, 15 cm<sup>3</sup> of water, 8.03 g of crotyl chloride and

a further 20 cm<sup>3</sup> of methanol are successively charged to a 150 cm<sup>3</sup> round-bottomed glass flask.

The heterogeneous mixture is stirred and becomes gradually dark brown and cloudy. The solution is subsequently treated with stirring with a gentle stream of carbon monoxide (bubble by bubble) for one hour. The mixture becomes clearer and a yellow precipitate appears. The stirring and the stream of CO are halted, the solution is left standing for one hour and then it is poured into 300 cm<sup>3</sup> of water and extracted with 5 times 50 cm<sup>3</sup> of chloroform. The resulting straw-yellow organic phase is washed with 2 times 100 cm<sup>3</sup> of water and dried over disodium sulphate overnight, and then the solvent is evaporated. 3.35 g of a pale yellow solid are thus recovered, the solid having a purity of greater than 94% (quantitative determination by Nuclear Magnetic Resonance: NMR).

#### 2) Hydroxycarbonylation of chlorobutene

The following are charged to a glass flask:

Chlorobutene                      5.0 g

Chlorocrotyl palladium      10.3 mg

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 130°C with shaking. When the preset temperature is reached,

the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to maintain a constant pressure.

After 60 minutes, the autoclave is cooled in a water bath to 20°C and then degassed. The homogeneous reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

RY (P3) = 12.7%

10 RY (P2) = 4.4%

The remainder is very predominantly chlorobutene.

2.09 g of the solution thus obtained are placed in a glass flask and 95 mg of Ceca L3S charcoal are added. Two purges under 15 bar of hydrogen are carried out and the mixture is shaken under 20 bar of H<sub>2</sub> and heated to 80°C. Once the temperature has been reached, a pressure of 40 bar of hydrogen is applied for 60 minutes. The autoclave is degassed and the reaction medium is filtered.

Quantitative determination of the palladium on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that 100% of the palladium charged to the reaction is recovered on the charcoal.

Example 10

The following are charged to a glass flask:

|                    |        |
|--------------------|--------|
| Pentanoic acid     | 10.0 g |
| Butadiene          | 2.6 g  |
| Chlorobutene       | 0.30 g |
| Water              | 0.92 g |
| Palladium acetate  | 0.11 g |
| Charcoal, Ceca L3S | 1.0 g  |

The glass flask is introduced into a 125 ml autoclave. The latter is immediately pressurized to  
5 100 bar of CO at ambient temperature. The autoclave is placed in an oven and the mixture is heated to 140°C with shaking. When the preset temperature is reached, the CO pressure is brought to 200 bar and the autoclave is placed in communication with a source of CO to  
10 maintain a constant pressure. The CO consumption is estimated with respect to the difference in pressure measured in the source.

At the end of the reaction, the autoclave is cooled in a water bath to 20°C and then slowly  
15 degassed. Five purges are carried out under 60 bar of hydrogen (the CO concentration falling to 0.05 ml per litre of solution). The mixture is then heated at 140°C under 70 bar of hydrogen with stirring for thirty-five minutes. After cooling and degassing, the reaction  
20 medium is filtered. The charcoal recovered is dried

before analysis. The reaction mass is analysed by high performance liquid chromatography (HPLC) and gas chromatography (GC).

The following results were obtained:

5

CY (pentanoic acid) = 93%

CY (diacids) = 3.0%

CY (2-methyl-3-butanoic acid) = 3.9%

Quantitative determination of the palladium on the charcoal collected and in the reaction mass after filtration is carried out by ICP-OES or ICP-MS. The results show that nearly 100% of the palladium charged to the reaction is recovered on the charcoal, 0.025% being found in the dissolved form in the reaction medium.

10

CLAIMS

1. Process for the preparation of unsaturated or saturated carboxylic acids [sic] from compounds comprising an ethylenic or acetylenic unsaturation conjugated with another unsaturation or an electron-donating group by reaction of carbon monoxide and water in the presence of a palladium-based catalyst, characterized in that it consists in treating the reaction medium, after the end of the hydroxycarbonylation reaction, by extraction of the carbon monoxide from the said reaction medium by treatment with a gas, in order to obtain a CO concentration of less than 600 ml of CO per litre of solution, then treatment of [sic] the reaction medium with hydrogen to reduce the palladium to the zero oxidation state and in separating the precipitated palladium from the reaction medium.

2. Process according to claim 1, characterized in that the concentration of carbon monoxide in the reaction medium before the stage of treatment with hydrogen is less than 10 mmol/l.

3. Process according to claim 2, characterized in that the concentration of carbon monoxide in the reaction medium before the stage of

treatment with hydrogen is between 0.001 ml/l and 600 ml/l.

4. Process according to one of claims 1 to 3, characterized in that the gas for entrainment of the carbon monoxide is chosen from the group consisting of nitrogen, the rare gases or hydrogen.

5. Process according to one of claims 1 to 4, characterized in that the stage of reduction of the palladium to the zero oxidation state is carried out under a hydrogen pressure of between 1 bar and 100 bar.

6. Process according to one of claims 1 to 5, characterized in that the stage of reduction of the palladium to the zero oxidation state is carried out at a temperature of between 20°C and 150°C.

7. Process according to one of the preceding claims, characterized in that a compound which is insoluble in the reaction medium is added to the said medium and then separated from the said medium after the stage of reduction of the palladium to the zero oxidation state.

8. Process according to claim 7, characterized in that the compound which is insoluble in the reaction medium is chosen from the group consisting of active charcoals, alumina, silica, zirconia, cerium oxide, polystyrene foams and silicone oils.

9. Process according to claim 7 or 8, characterized in that the compound which is insoluble in the reaction medium is added at the beginning of the reaction.

10. Process according to claim 7 or 8, characterized in that the compound which is insoluble in the reaction medium is added before the stage of reduction of the palladium.

11. Process according to one of the preceding claims, characterized in that the compounds comprising a conjugated ethylenic unsaturation are chosen from the group consisting of diolefins, allyl alcohols, allyl ethers, allyl esters and allyl halides.

12. Process according to claim 11, characterized in that the diolefin is butadiene.

13. Process according to one of claims 7 to 12, characterized in that the palladium deposited on the insoluble compound is recovered by treatment of the said insoluble compound after separation from the reaction medium.

14. Process according to claim 13, characterized in that the treatment of the insoluble compound comprising the reduced palladium is a dissolution of the palladium by attack by a strong acid.