

The subject of the present invention is a process for the preparation of hexene-1,6-dioic acid diesters. These diesters may be hydrogenated to the corresponding adipic acid diesters or adipates, which may then be hydrolysed in order to form adipic acid. Adipic acid, one of the starting materials for nylon 66, is produced in heavy tonnages and, by this fact alone, any new route of access to this diacid and/or to its derivatives presents an advantage which is, in principle, immediately apparent.

More specifically, the subject of the present invention is a process for the preparation of 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide with at least one 1,2-dialkoxy-3-butene in the presence of a palladium-based catalyst.

It has already been proposed by IMAMURA and TSUJI, Tetrahedron, vol. 25, p. 4187-4195 (1969) to prepare 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide with 1,4-diethoxy-2-butene in ethanol, in the presence of palladium and of chloride.

1,2-Diethoxy-3-butene is mentioned as a co-product and is assumed to originate from an allylic rearrangement of 1,4-diethoxy-2-butene.

It has also been proposed (cf. US-A-4,611,082) to dicarbonylate a 1,4-dialkoxy-2-butene in a polar aprotic and non-basic solvent, at 80-140°C in the presence of a transition metal halide, palladium chloride proving to be the most effective.

This same type of reaction formed the subject of a detailed study starting from 1,4-dimethoxy-2-butene, published in "Journal of Molecular Catalysis, 53 (1989) p. 417-432".

Now, the research carried out in parallel by the Applicant, regarding the preparation of dialkoxybutenes from 1,3-butadiene, has shown that a mixture in particular containing 1,4-dialkoxy-2-butene (major ether) and 1,2-dialkoxy-3-butene is generally obtained during this preparation, these two diethers being relatively difficult to separate from each other.

It has now been found that it is possible to prepare 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide with at least one 1,2-dialkoxy-3-butene in the presence of a palladium-based catalyst.

5 The subject of the present invention is thus a process for the preparation of 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide with at least one dialkoxybutene in the presence of a palladium-based catalyst and a halogenated compound, in the liquid phase,
10 at high temperature and under a pressure greater than atmospheric pressure, characterized in that the dialkoxy-butene is a 1,2-dialkoxy-3-butene.

 1,2-Dialkoxy-3-butene, in the context of the present process, is understood to refer to 3-butenes
15 disubstituted in positions 1 and 2 with identical or different, linear, branched or cyclic alkoxy groups and containing from 1 to 12 carbon atoms. The two alkoxy groups are preferably identical and they advantageously contain from 1 to 4 carbon atoms. 1,2-Dimethoxy-3-butene
20 and 1,2-dethoxy-3-butene are particularly appropriate starting materials, in the context of the present process.

 According to an advantageous variant of the process according to the invention, the 1,2-dialkoxy-3-
25 butene(s) is (are) used in the form of a mixture with the 1,4-dialkoxy-2-butene(s), in which they may represent a variable molar fraction, for example from 5 to 99 % of the said mixture.

 It has, in fact, been surprisingly found that the
30 selectivity towards linear diester required (linear dicarbonylated product) starting from these branched diethers (1,2-dialkoxy-3-butene), whether they are employed individually or mixed with the corresponding linear diethers, is sufficiently high in the context of
35 the present process to envisage the use as starting material of the mixture of the branched diether and the linear diether in the proportions in which they are present during the step for their preparation from 1,3-butadiene.

 The process according to the present invention is

carried out in the presence of a palladium-based catalyst.

Although the precise nature of the catalytically active species in the reaction in question has not been
5 entirely elucidated, the Applicant presumes that various palladium compounds and palladium metal are capable of being useful precursors in the implementation of the present process.

Among the sources of palladium which may be used
10 for performing the process forming the subject of the invention, there may be mentioned:

- palladium metal deposited, where appropriate, on a support such as carbon, alumina or silica,
- PdCl_2 , $\text{Pd}(\text{OAc})_2$,
- 15 • π -allylic palladium complexes or salts, in which the anion coordinated to the Pd cation is chosen from the following anions: carboxylates such as formate, acetate, propionate or benzoate; acetylacetonate, halides such as Cl^- and Br^- , and prefer-
20 ably Cl^- ;

Use is advantageously made of palladium chloride.

The precise amount of catalyst to be used, which may vary within a wide range, will above all depend on a compromise between the desired efficiency and the expense
25 on catalyst and on the other conditions chosen for the reaction. Good results may generally be obtained with a palladium concentration in the reaction medium between 10^{-3} and 1 mol/l. Below 10^{-3} mol/l, the reaction kinetics are slowed down considerably. Amounts of palladium
30 greater than 1 mol/l have no disadvantages other than from the economic point of view. This concentration is preferably between 10^{-2} and 1 mol/l.

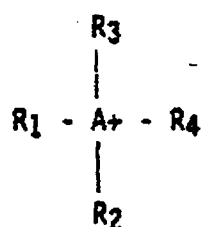
The process according to the present invention is also carried out in the presence of a halogenated com-
35 pound. The Applicant more particularly recommends that use be made of an ionic chloride in which the cation is chosen from the group consisting of

- a) alkali metal cations,
- b) alkaline-earth metal cations, and

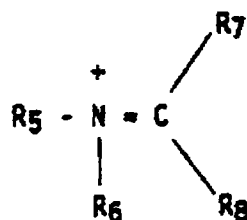
- c) quaternary onium cations of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, the nitrogen being able to be coordinated to two pentavalent phosphorus atoms.
- 5

For good implementation of the process according to the invention, the quaternary onium chloride will have a quaternary onium cation corresponding to one of the formulae (I) to (V) below:

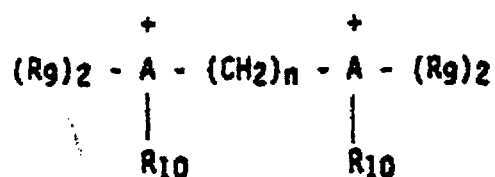
I)



II)

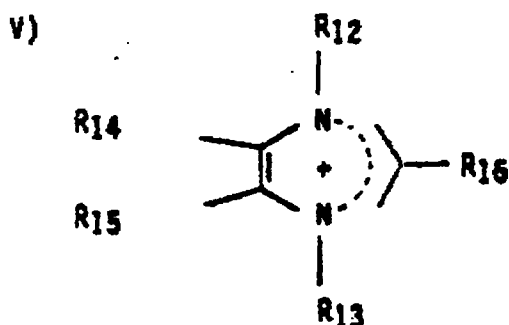


III)



IV)





in which formulae:

- A represents nitrogen or phosphorus

- R₁, R₂, R₃ and R₄ are identical or different and represent:

5 • a linear or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halo, nitro, alkoxy or alkoxycarbonyl group;

 • a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms,

10 • an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl radical(s) containing 1 to 4 carbon atoms, or alkoxy, alkoxycarbonyl or haloradicals;

 • two of the said radicals R₁ to R₄ being able jointly to form a linear or branched alkylene, alkenylene or alkadienylene radical containing 3 to 6 carbon atoms;

- R₅, R₆, R₇ and R₈ are identical or different and represent:

20 • a linear or branched alkyl radical containing 1 to 4 carbon atoms;

 • the radicals R₇ and R₈ being able jointly to form an alkylene radical containing 3 to 6 carbon atoms;

25 • the radicals R₆ and R₇ or R₆ and R₈ being able jointly to form an alkylene, alkenylene or an alkadienylene radical containing 4 carbon atoms and constituting with N a nitrogenous heterocycle;

- R₉ represents a linear or branched alkyl radical containing 1 to 4 carbon atoms, or a phenyl radical;

- R₁₀ represents:

30 • a linear or branched alkyl radical containing 1 to 4 carbon atoms, similar to or different from R₉;

• a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms;

• n represents an integer greater than or equal to 1 and less than or equal to 10, and preferably less than or equal to 6;

• R_{11} represents an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl group(s) containing 1 to 4 carbon atoms, or alkoxy, alkoxy carbonyl or halo groups;

• R_{12} and R_{13} are identical or different and have the meaning given earlier for R_1 to R_4 ;

• R_{14} to R_{16} are identical or different and represent:

• a hydrogen atom

• a linear or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halo, nitro, alkoxy, or alkoxy carbonyl group;

• a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms,

• an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl radical(s) containing 1 to 4 carbon atoms, or alkoxy, alkoxy carbonyl or halo radicals;

• the radicals R_{14} and R_{15} may jointly form a linear or branched alkylene, alkenylene or alkadienylene radical containing 3 to 6 carbon atoms; they can thus constitute, with the 2 adjacent carbon atoms of the imidazole ring, an aromatic ring.

By way of example of quaternary onium cations corresponding to the formula I, there may be mentioned the cations:

- tetramethylammonium,
- triethylmethylammonium
- tributylmethylammonium
- trimethyl(n-propyl)ammonium
- tetraethylammonium
- tetrabutylammonium
- dodecyltrimethylammonium
- methyltrioctylammonium

- heptyltributylammonium
- tetrapropylammonium
- tetrapentylammonium
- tetrahexylammonium
- 5 • tetraheptylammonium
- tetraoctylammonium
- tetradecylammonium
- butyltripropylammonium
- methyltributylammonium
- 10 • pentyltributylammonium
- methyldiethylpropylammonium
- ethyldimethylpropylammonium
- tetradodecylammonium
- tetraoctadecylammonium
- 15 • hexadecyltrimethylammonium
- benzyltrimethylammonium
- benzyldimethylpropylammonium
- benzyldimethyloctylammonium
- benzyltributylammonium
- 20 • benzyltriethylammonium
- phenyltrimethylammonium
- benzyldimethyltetradecylammonium
- benzyldimethylhexadecylammonium
- dimethyldiphenylammonium
- 25 • methyltriphenylammonium
- 2-butenyltriethylammonium
- N,N-dimethyltetramethylenammonium
- N,N-diethyltetramethylenammonium
- tetramethylphosphonium
- 30 • tetrabutylphosphonium
- ethyltrimethylphosphonium
- trimethylpentylphosphonium
- octyltrimethylphosphonium
- dodecyltrimethylphosphonium
- 35 • trimethylphenylphosphonium
- diethyldimethylphosphonium
- dicyclohexyldimethylphosphonium
- dimethyldiphenylphosphonium
- cyclohexyltrimethylphosphonium

- triethylmethylphosphonium
- methyltri(isopropyl)phosphonium
- methyltri(n-propyl)phosphonium
- methyltri(n-butyl)phosphonium
- 5 • methyltri(2-methylpropyl)phosphonium
- methyltricyclohexylphosphonium
- methyltriphenylphosphonium
- methyltribenzylphosphonium
- methyltri(4-methylphenyl)phosphonium
- 10 • methyltriisobutylphosphonium
- diethylmethylphenylphosphonium
- dibenzylmethylphenylphosphonium
- ethyltriphenylphosphonium
- tetraethylphosphonium
- 15 • ethyltri(n-propyl)phosphonium
- triethylpentylphosphonium
- hexadecyltributylphosphonium
- ethyltriphenylphosphonium
- n-butyltri(n-propyl)phosphonium
- 20 • butyltriphenylphosphonium
- benzyltriphenylphosphonium
- (β-phenylethyl)dimethylphenylphosphonium
- tetraphenylphosphonium
- triphenyl(4-methylphenyl)phosphonium
- 25 • tetrakis(hydroxymethyl)phosphonium
- tetrakis(2-hydroxyethyl)phosphonium

Among the cations corresponding to the formula
II, there may be mentioned the cations:

- N-methylpyridinium
- 30 • N-ethylpyridinium
- N-hexadecylpyridinium
- N-methylpicolinium

Among the cations corresponding to the formula
III, there may be mentioned the cations:

- 35 • 1,2-bis(trimethylammonium)ethane
- 1,3-bis(trimethylammonium)propane
- 1,4-bis(trimethylammonium)butane
- 1,3-bis(trimethylammonium)butane

Among the cations corresponding to the formula

IV, there may be mentioned the cations:

- bis(triphenylphosphine)iminium
- bis(tritolylphosphine)iminium.

Among the cations corresponding to the formula V,
5 there may be mentioned the cations:

- 1-methyl-3-methylimidazolium
- 1-methyl-3-ethylimidazolium
- 1-methyl-3-n-propylimidazolium
- 1-methyl-3-n-butylimidazolium
- 10 • 1-methyl-3-benzylimidazolium
- 1-methyl-2-methyl-3-benzimidazolium.

Use is advantageously made of those of the onium
cations corresponding to the formula (I) above in which:

- A represents phosphorus, and
- 15 - R₁, R₂, R₃ and R₄ are identical or different and
represent a linear or branched alkyl radical containing
from 1 to 8 carbon atoms or a phenyl or 4-methylphenyl
radical.

A tetraalkylphosphonium chloride is preferably
20 used.

Tetrabutylphosphonium chloride, which is avail-
able and particularly effective, is more especially
recommended.

It will be noted that certain palladium com-
pounds, such as PBu₄PdCl₃, may constitute both a source of
25 palladium and a means of introducing at least a part of
the quaternary ammonium chloride in the sense indicated
above.

As indicated above, the process according to the
30 present invention may be implemented by using [lacuna] as
ionic alkali metal or alkaline-earth metal chloride. By
way of examples of such chlorides, there may be mentioned
LiCl and CaCl₂, LiCl proving to be more particularly
effective.

35 Of course, it is possible, in the context of the
present invention, to use a mixture of inorganic
chlorides and/or of quaternary onium chlorides in the
sense recalled at the start of the present specification.

It has already been proposed in EP-A-347 340 to

prepare 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide and an alcohol with at least one butene disubstituted by acyloxy groups in the presence of a palladium-based catalyst and a quaternary onium chloride
5 corresponding to the formulae I to IV above.

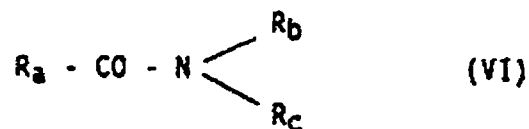
The amount of ionic chloride to be employed in the reaction medium will generally be such that the Cl⁻/Pd molar ratio is greater than or equal to 1, this ratio only having upper limits on the grounds of economic
10 constraints and/or of handling difficulties of the reaction medium.

The said molar ratio is preferably between 3 and 100.

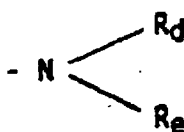
The reaction medium may, where appropriate, contain an organic solvent or diluent. When it is desired
15 to work in the presence of a solvent or diluent, use is made of polar, aprotic, basic or non-basic solvents. Among the polar, aprotic non-basic solvents which are suitable for implementing the invention, nitriles such as
20 acetonitrile will be mentioned.

When it is chosen to make use only of alkali metal or alkaline-earth metal chlorides, it proves useful to carry out the reaction in a polar, aprotic and preferably basic solvent.

25 Polar, aprotic and basic solvent is understood by the Applicant to refer to the compounds of formula (VI):



in which R_a, R_b and R_c, which may be identical or different, represent an alkyl radical, a cycloalkyl radical, an aralkyl radical or a monocyclic aryl radical
30 having not more than 10 carbon atoms, two radicals R_a, R_b or R_c being able jointly to constitute a single divalent radical - (CH₂)_y -, y being an integer between 3 and 12, and R_a being able, in addition, to represent a radical



in which R_d and R_e , which may be identical or different, represent an alkyl radical having at most 4 carbon atoms.

By way of example of such solvents, there may be mentioned:

tetramethylurea, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-dicyclohexylacetamide, N,N-dimethylpropionamide, N,N-diethylpropionamide, N,N-diethyl-n-butyramide, N,N-dimethylbenzamide, N,N-dicyclohexylbenzamide, N,N-diethyl-m-toluamide, N-acetylpyrrolidine, n-acetyl-
piperidine, N-(n-butyryl)piperidine, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, N-methyl-2-piperidone and N-methyl-epsilon-caprolactam.

N-Methyl-2-pyrrolidone is particularly suitable for implementing the present process.

When use is made of a solvent, its amount represents at least 10 % by volume of the reaction medium; good results are obtained when an amount thereof of the order of 20 % to 90 % by volume is used.

The reaction will generally be able to be carried out in the liquid phase at a temperature between 50 and 180°C, preferably between 80 and 150°C, under a pressure of carbon monoxide greater than or equal to 20 bar, and preferably less than or equal to 250 bar.

For good implementation of the invention, the pressure of carbon monoxide will preferably be between 90 and 180 bar.

Inert gases such as nitrogen, argon or carbon dioxide may be present along with the carbon monoxide.

At the end of the reaction or of the time allotted to the reaction, the diester required is recovered by any appropriate means, for example by extraction and/or distillation.

The examples below illustrate the invention.

Examples 1 to 5; Control tests (a) to (d):

The following are introduced into a 20 cm³ stain-

less steel autoclave (Hastelloy B2), flushed beforehand with argon:

- 8.7 mmol of 1,2-dimethoxy-3-butene
- 1.66 mg-at. of palladium in the form of PdCl_2
- 5 • 6 mmol of ionic chloride
- where appropriate, 10 cm^3 of solvent.

The autoclave is hermetically closed, placed in an oven incorporating agitation and connected to the supply of gas under pressure. The reactor is flushed while cold with carbon monoxide and is brought to 95°C. 10 The pressure is subsequently adjusted to 140 bar. After reaction, the autoclave is cooled and degassed.

The reaction mixture is then analysed by gas chromatography.

15 The specific conditions and the results obtained are featured in Table I below, in which t represents the reaction time at the given temperature, HD (%) represents the molar amount of methyl 3-hexenedioate formed per 100 moles of 1,2-dimethoxy-3-butene charged, and 20 DC (%) represents the degree of conversion of the 1,2-dimethoxy-3-butene.

DMI Cl = N,N-dimethylimidazolium chloride

NMP = N-methyl-2-pyrrolidone

p-DCB = para-dichlorobenzene

25

TABLE I

Ref.	Ionic chloride	Solvent	t (h)	DC (%)	3HD (%)
1	PBu_4Cl	none	6	100	80
2	PBu_4Cl	NMP	6	100	92.5
3	LiCl	NMP	6	100	86
30 4	NMe_4Cl	NMP	6	100	82
5	DMICl	NMP	6	100	91
a	none	ethanol	6	100	3
b	none	acetonitrile	6	37	8
c	none	NMP	6	57	9
35 d	none	p-DCB	6	100	38

Examples 6 and 7

The following are introduced into a 125 cm³ stainless steel autoclave (Hastelloy B2), flushed beforehand with argon:

- 5 - 25 mmol of 1,2-dimethoxy-3-butene
 - 5 mmol of palladium in the form of PdCl₂,
 - tetrabutylphosphonium chloride, and
 - where appropriate, 30 cm³ of solvent.

10 The autoclave is then closed and the process is performed as described for Examples 1 to 5 (T = 95°C; P = 140 bar).

The specific conditions and the results obtained are collated in Table II below:

TABLE II

15

Ref.	PBu ₄ Cl	Solvent	t (h)	DC (%)	3HD (%)
6	5	acetonitrile	8	96	72
7	27	none	8	99	80

Examples 8 and 9:

20 Example 7 is repeated, in an autoclave and according to the experimental procedure described above, on a charge which is modified as follows:

- a mixture of 1,4-dimethoxy-2-butene (1,4-DMB) and 1,2-dimethoxy-3-butene (1,2-DMB) is introduced
 - 19 mmol of PBu₄Cl are introduced,

25 The specific conditions and the results obtained are collated in Table III below:

TABLE III

30

Ref.	1,4-DMB mmol	1,2-DMB mmol	t (h)	3HD (%)
8	18.5	8	4.8	65
9	8	17.5	5.7	74

In these 2 tests, the conversion of the

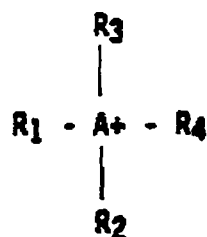
dimethoxybutenes is total.



CLAIMS

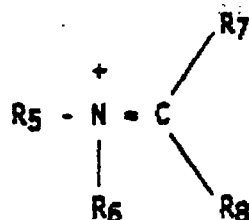
1. Process for the preparation of 3-hexene-1,6-dioic acid diesters by reaction of carbon monoxide with at least one dialkoxybutene in the presence of a palladium-based catalyst and a halogenated compound, in the liquid phase, at high temperature and under a pressure greater than atmospheric pressure, characterized in that the dialkoxybutene is a 1,2-dialkoxy-3-butene.
2. Process according to claim 1, characterized in that a mixture of 1,2-dialkoxy-3-butene and 1,4-dialkoxy-2-butene is employed in the reaction.
3. Process according to claim 1 or 2, characterized in that the halogenated compound is an ionic chloride whose cation is chosen from the group consisting of
- a) alkali metal cations,
 - b) alkaline-earth metal cations, and
 - c) quaternary onium cations of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, the nitrogen being able to be coordinated to two pentavalent phosphorus atoms.
4. Process according to any one of the preceding claims, characterized in that the halogenated compound is a quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, the nitrogen being able to be coordinated to two pentavalent phosphorus atoms.
5. Process according to claim 1 or 2, characterized in that the quaternary onium cation corresponds to one of the following formulae (I) to (V):

I)

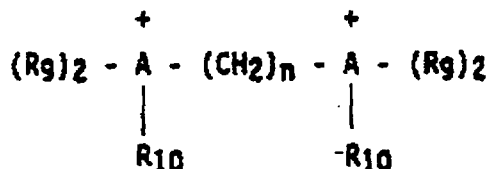




II)



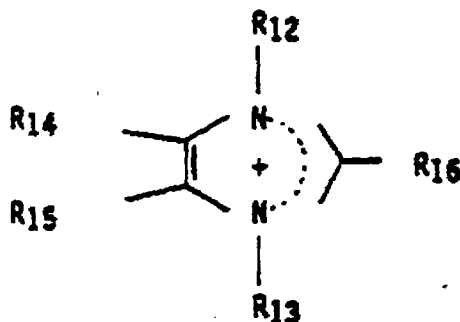
III)



IV)



V)



in which formulae:

- A represents nitrogen or phosphorus

- R_1 , R_2 , R_3 and R_4 are identical or different and represent:

5 • a linear or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halo, nitro, alkoxy or alkoxycarbonyl group;

 • a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms,

10 • an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl radical(s) containing 1 to 4 carbon atoms, or alkoxy, alkoxycarbonyl or halo radicals;

 • two of the said radicals R_1 to R_4 being able



jointly to form a linear or branched alkylene, alkenylene or alkadienylene radical containing 3 to 6 carbon atoms;

- R_5 , R_6 , R_7 and R_8 are identical or different and represent:

5 • a linear or branched alkyl radical containing 1 to 4 carbon atoms;

 • the radicals R_7 and R_8 being able jointly to form an alkylene radical containing 3 to 6 carbon atoms;

10 • the radicals R_6 and R_7 or R_6 and R_8 being able jointly to form an alkylene, alkenylene or an alkadienylene radical containing 4 carbon atoms and constituting with N a nitrogenous heterocycle;

 - R_9 represents a linear or branched alkyl radical containing 1 to 4 carbon atoms, or a phenyl radical;

15 - R_{10} represents:

 • a linear or branched alkyl radical containing 1 to 4 carbon atoms, similar to or different from R_9 ;

 • a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms;

20 - n represents an integer greater than or equal to 1 and less than or equal to 10, and preferably less than or equal to 6;

 - R_{11} represents an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl group(s) containing 1 to 4 carbon atoms, or alkoxy, alkoxy carbonyl or halo groups;

25 - R_{12} and R_{13} are identical or different and have the meaning given earlier for R_1 to R_4 ;

30 - R_{14} to R_{16} are identical or different and represent:

 • a hydrogen atom

 • a linear or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halo, nitro, alkoxy, or alkoxy carbonyl group;

35 • a linear or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms,

 • an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl radical(s) containing 1 to 4 carbon atoms, or alkoxy,



alkoxycarbonyl or halo radicals;

the radicals R_{14} and R_{15} may jointly form a linear or branched alkylene, alkenylene or alkadienylene radical containing 3 to 6 carbon atoms; they can thus constitute, with the 2 adjacent carbon atoms of the imidazole ring, an aromatic ring.

6. Process according to claim 5, characterized in that the quaternary onium cation corresponds to the formula (I) in which:

- A represents phosphorus, and
- R_1 , R_2 , R_3 and R_4 are identical or different and represent a linear or branched alkyl radical containing 1 to 8 carbon atoms, a phenyl radical or a 4-methylphenyl radical.

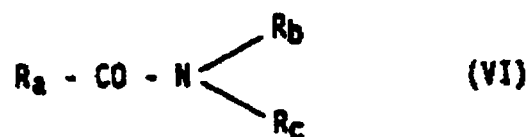
7. Process according to any of the preceding claims, characterized in that the halogenated compound is tetrabutylphosphonium chloride.

8. Process according to any one of claims 1 to 3, characterized in that the halogenated compound is an alkali metal chloride or an alkaline-earth metal chloride.

9. Process according to any one of claims 1 to 3, characterized in that the halogenated compound is lithium chloride.

10. Process according to either of claims 8 and 9, characterized in that the reaction is performed in an aprotic and basic polar solvent.

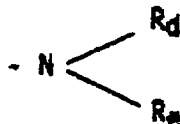
11. Process according to claim 10, characterized in that the solvent is chosen from the compounds of formula (VI):



in which R_a , R_b and R_c , which may be identical or different, represent an alkyl radical, a cycloalkyl radical, an aralkyl radical or a monocyclic aryl radical having not more than 10 carbon atoms, two radicals R_a , R_b or R_c being able jointly to constitute a single divalent



radical - $(CH_2)_y$ -, y being an integer between 3 and 12,
and R_a being able, in addition, to represent a radical



in which R_d and R_a , which may be identical or different,
represent an alkyl radical having at most 4 carbon atoms.

- 5 12. Process according to claim 10 or 11, characterized in that the quantity of solvent represents at least 10% by volume of the reaction mixture.
- 10 13. Process according to any one of claims 10 to 12, characterized in that the solvent is N-methyl-2-pyrrolidone.
- 15 14. Process according to any one of the preceding claims, characterized in that the molar ratio of the chloride anion to the palladium is between 3 and 100.
- 15 15. Process according to any one of the preceding claims, characterized in that the palladium concentration in the reaction mixture is between 10^{-3} and 1 mol/l.
- 20 16. Process according to any one of the preceding claims, characterized in that the reaction temperature is between 50 and 180°C, and preferably between 80 and 150°C.
17. Process according to any one of the preceding claims, characterized in that the pressure is greater than or equal to 20 bar, and preferably less than or equal to 250 bar.
- 25 18. Process according to any one of the preceding claims, characterized in that the pressure is between 90 and 180 bar.
19. Process according to any one of the preceding claims, characterized in that the palladium is employed
- 30 in the form of palladium chloride.