

The present invention relates to a process for linear dicarbonylation of difunctionalized butenes. Linear dicarbonylation means the predominant formation of 3-hexene-1,6-dioic acid and/or of its dialkyl esters, by reaction of carbon monoxide, if appropriate of an alcohol, with at least one butene disubstituted by hydroxyl, alkoxy or acyloxy groups.

Diesters of 3-hexene-1,6-dioic acid can be hydrogenated to the corresponding diesters of adipic acid, which can then be hydrolysed to form adipic acid.

3-Hexene-1,6-dioic acid can be hydrogenated to adipic acid.

Adipic acid, one of the raw materials for nylon 66, is produced in high tonnages and, owing to this fact alone, any new route of access to this diacid and/or to its derivatives is of fundamental interest as can be immediately appreciated.

In European Patent Application EP-A-0 347 340 (corresponding to US Patent 4 925 973) a catalytic process was proposed for the preparation of diesters of 3-hexene-1,6-dioic acid by reaction of carbon monoxide and of an alcohol with at least one butene disubstituted by acyloxy groups. The linear dicarbonylation is carried out in the presence of a catalyst based on palladium and on a quaternary onium halide of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, it being possible for the nitrogen to be coordinated to 2 pentavalent phosphorus atoms, the halide anion being chosen from chloride and bromide. Such a process makes it possible to carry out the carbonylation under pressure and temperature conditions which are acceptable on an industrial scale, with an appreciable selectivity for a linear dicarbonylated product, the proportions of monocarbonylated product and of branched dicarbonylated products being very small.

In European Patent Application EP-A-0 395 545 a catalytic process was proposed for the preparation of 1,6-hexenedioic acid by reaction of carbon monoxide and water with at least one butene disubstituted by acyloxy

groups. The linear dicarbonylation is also carried out in the presence of a catalyst based on palladium and on a quaternary onium chloride within the meaning indicated above.

5 Example 8 of this application, carried out with metallic palladium deposited on charcoal and in the presence of tetrabutylphosphonium chloride, does not produce results which are entirely satisfactory.

10 In European Patent Application EP-A-0 395 546 a catalytic process was proposed in particular for the preparation of 3-hexene-1,6-dioic acid by reaction of carbon monoxide and of 2-butene-1,4-diol and/or of 1-butene-3,4-diol.

15 The linear dicarbonylation is carried out in the presence of a catalyst based on palladium and on a quaternary onium chloride within the abovementioned meaning.

20 Example 21 of this application, carried out with metallic palladium deposited on charcoal in the presence of tetrabutylphosphonium chloride, does not produce results which are fully satisfactory.

25 In the European Patent Applications filed under numbers 90/322 256, 90/322 257 and 90/322 258 respectively it was proposed to replace the onium halide within the abovementioned meaning at least partially by the pair made up of certain inorganic halides and of a basic aprotic polar solvent.

30 In French Patent Application filed under number 90/12042 another catalytic process was proposed for the preparation of diesters of 3-hexene-1,6-dioic acid by reaction of carbon monoxide with a 1,2-dialkoxy-3-butene taken in isolation or mixed with a 1,4-dialkoxy-2-butene.

35 The linear dicarbonylation is carried out in the presence of a catalyst based on palladium and on an ionic chloride in which the cation is chosen from the group consisting of alkali metal cations, alkaline-earth metal cations and quaternary onium cations within the meaning stated above.

 However, all of these catalytic processes for

linear dicarbonylation of difunctionalized butenes - the fundamental advantage of which is not questioned - exhibit at least one of the following disadvantages:

- certain sources of palladium, and in particular
5 metallic palladium deposited on a support, do not exhibit a fully satisfactory activity under certain conditions;
- the catalyst system exhibits an insufficient stability with time, and this can be reflected in
10 palladium being seen to precipitate on the walls and bottom of the carbonylation reactor.

It would therefore be highly desirable to have available a catalytic process for linear dicarbonylation of difunctionalized butenes, in which the palladium-based catalyst system has an improved stability and, if appropriate, an improved catalyst activity.
15

The subject of the present invention is therefore a process for linear dicarbonylation of difunctionalised butenes in the presence of a catalytically effective quantity of palladium and of a quaternary onium chloride
20 of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, it being possible for the nitrogen to be coordinated to 2 pentavalent phosphorus atoms, in liquid phase, at elevated temperature and at a pressure above
25 atmospheric pressure, characterised in that

a) the palladium is introduced at least partially in the form of palladium in the zero oxidation state and

b) the reaction is also conducted in the presence of at least one source of hydrogen chloride.

30 As indicated at the beginning of this specification, one of the raw materials employed within the scope of the present process is at least one butene which is difunctionalized, that is to say disubstituted by hydroxyl, alkoxy or acyloxy groups, be it 2-butene
35 substituted in positions 1 and 4 or 3-butene substituted in positions 1 and 2. These difunctionalized butenes may be denoted by either of the formulae hereinbelow:



in which Z denotes an -OH, -OR or -O-(CO)-R group; R is a linear, branched or cyclic alkyl radical which contains from 1 to 12 carbon atoms and preferably from 1 to 4 carbon atoms.

5 As examples of difunctionalized butenes which can be used within the scope of the present process there may be mentioned:

- 2-butene-1,4-diol 3-butene-1,2-diol and their mixtures

10 - 1,4-dimethoxy-2-butene, 1,2-dimethoxy-3-butene and their mixtures

- 1,4-diethoxy-2-butene, 1,2-diethoxy-3-butene and their mixtures

15 - 1,4-diacetoxy-2-butene, 1,2-diacetoxy-3-butene and their mixtures

Although in principle there is nothing against choosing a mixture of various raw materials from among the said disubstituted butenes, in practice it has proved more advantageous to chose mixtures of diols, mixtures of dialkoxybutenes or mixtures of diacyloxybutenes.

20 The Applicant Company has found, in fact, that the selectivity for a linear dicarbonylation product is substantially the same whether the starting material is a 2-butene disubstituted in positions 1 and 4 or a 3-butene disubstituted in positions 1 and 2, by a given type of substituent.

3-Hexene-1,6-dioic acid will be obtained as predominant product from butenediol(s) and carbon monoxide by using the process according to the invention.

30 The corresponding alkyl 3-hexenedioate will be obtained as predominant product from dialkoxybutene(s) and carbon monoxide by using the process according to the invention.

35 3-Hexene-1,6-dioic acid will be obtained as predominant product from diacyloxybutene(s), carbon

monoxide and water by using the process according to the invention.

3-Hexene-1,6-dioic acid and its alkyl esters, in proportions which can vary according to the reaction conditions, will be obtained as predominant products from diacyloxybutene(s), carbon monoxide and an alcanol by using the process according to the invention.

According to an essential characteristic of the present invention the dicarbonylation is carried out in the presence of palladium, used at least partially in the form of palladium in the zero oxidation state.

To do this, it is possible to use finely divided metallic palladium or metallic palladium deposited on a support such as silicas, aluminas, silico-aluminas, zirconia, quartz, clays and active carbons.

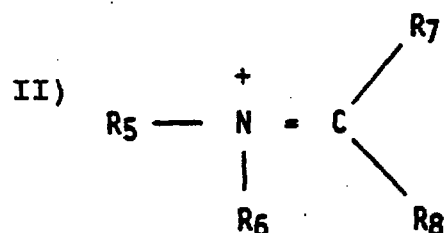
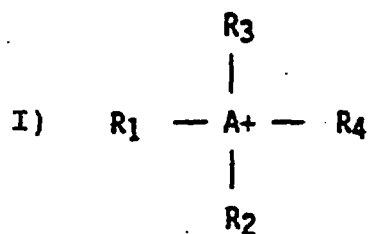
Palladium deposited on active carbon is more particularly suitable for the use of the present process.

The quantity of palladium deposited on the support can vary within wide limits. A quantity of between 1 and 10 % by weight appears to be an acceptable compromise between the economic constraints and the efficiency which is required.

The dicarbonylation is also conducted in the presence of a quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, it being possible for the nitrogen to be coordinated to 2 pentavalent phosphorus atoms.

The quaternary onium cations in question are well known to those skilled in the art, who will find it useful to refer to European Application EP-A-0 347 340, incorporated by reference.

A quaternary onium chloride is preferably used, in which the cation corresponds to one of the formulae (I) and (II) below:



in which:

- A denotes nitrogen or phosphorus
- 5 - R_1 , R_2 , R_3 and R_4 are identical or different and denote:
 - a linear or branched alkyl radical containing from 1 to 8 carbon atoms,
 - an aryl radical containing from 6 to 10 carbon atoms, optionally substituted by one or more alkyl radicals containing from 1 to 4 carbon atoms;
- R_5 , R_6 , R_7 and R_8 are identical or different and denote:
 - 15 - a linear or branched alkyl radical containing from 1 to 4 carbon atoms;
 - it being possible for the radicals R_7 and R_8 to form together an alkylene radical containing from 3 to 6 carbon atoms,
 - 20 - it being possible for the radicals R_6 and R_7 or R_6 and R_8 to form together an alkylene, alkenylene or alkadienylene radical containing 4 carbon atoms and forming a nitrogenous heterocyclic ring with N.
- 25 Use is advantageously made of a quaternary phosphonium chloride whose cation corresponds to the formula (I) above.

Tetrabutylphosphonium chloride, which is

available and particularly effective, is more especially recommended.

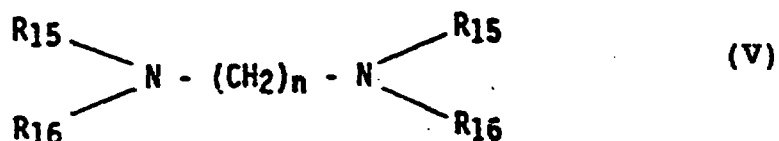
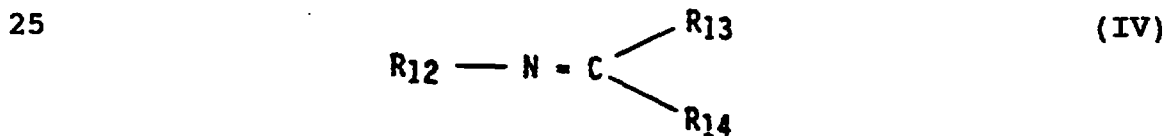
The onium cation/palladium molar ratio is generally between 0.5 and 150, the upper limit of the said ratio being dictated only by economic considerations. The said molar ratio is preferably between 5 and 150.

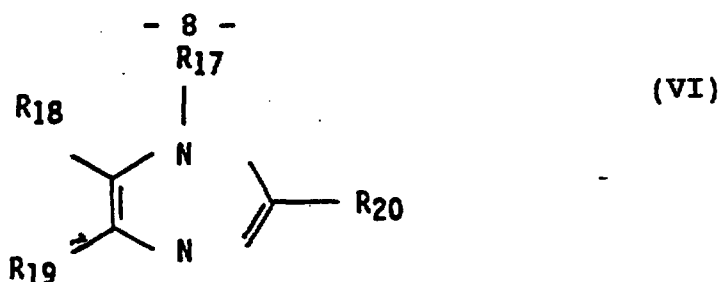
According to another essential characteristic of the present invention the dicarbonylation is carried out in the presence of at least one source of hydrogen chloride.

A source of hydrogen chloride means, within the scope of the present process, gaseous HCl, aqueous or organic solutions of HCl and organic chlorides capable of releasing HCl under the reaction conditions.

Of the organic chlorides, use is advantageously made of amine hydrochlorides, which are easy to handle and which, when it is desired to obtain predominantly alkyl esters of 3-hexene-1,6-dioic acid, do not result in the formation of an additional quantity of the said acid.

More specifically, the amine hydrochloride is derived from an amine corresponding to any one of the formulae (III) to (VI) below:





in which:

- R_9 to R_{11} are identical or different and denote:

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

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

an aryl radical containing from 6 to 10 carbon atoms, optionally substituted by one or more alkyl radicals containing from 1 to 4 carbon atoms, alkoxy, alkoxy carbonyl or halogen;

15 it being possible for two of the said radicals R_9 to R_{11} to form together a linear or branched alkylene, alkenylene or alkadienylene radical containing from 3 to 6 carbon atoms;

20 - R_{12} to R_{14} are identical or different and denote:

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

25 it being possible for the radicals R_{13} and R_{14} to form together an alkylene radical containing from 3 to 6 carbon atoms;

it being possible for the radicals R_{12} and R_{13} (or R_{12} and R_{14}) to form together an alkylene, alkenylene or alkadienylene radical containing 4 carbon atoms and forming a nitrogenous heterocyclic ring with N;

30 - R_{15} and R_{16} are identical or different and denote:

a hydrogen atom
35 a linear or branched alkyl radical containing from 1 to 4 carbon atoms;

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

n is an integer between 1 and 6 inclusive;

- 5 - R₁₇ has the meaning given above for R₁ to R₁₁;
 - R₁₈ to R₂₀ are identical or different and

denote:

a hydrogen atom;

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

- 15 a linear or branched alkenyl radical containing from 2 to 12 carbon atoms, preferably from 4 to 8 carbon atoms.

As examples of amines corresponding to the formula (III) there may be mentioned:

- ammonia,
mono-, di- and trimethylamines
20 mono-, di- and triethylamines
 mono-, di- and tri-n-propylamines
 mono-, di- and tributylamines
 mono-, di- and triisopropylamines
 mono-, di and tripentylamines
25 mono-, di- and trihexylamines
 mono-, di- and trioctylamines
 mono-, di- and tridodecylamines
 cyclohexylamine
 aniline
30 diphenylamine
 benzylamine
 triethanolamine
 diethylmethylaniline
 N,N-dimethylethanolamine
35 N,N-diethylaniline
 2,6-diethylaniline
 N,N-diethylcyclohexylamine
 dimethylaminobenzylamine
 N,N-dimethyl-2-chloroethylamine

pyrrolidine
2-chloroaniline
triethylenediamine
quinuclidine
5 1,2,3,4-tetrahydro-1-naphthylamine
piperazine

As examples of amines corresponding to the formula (IV) there may be mentioned:

pyridine
10 3-methylpyridine
2-phenylpyridine
indole
2-picoline
diazabicyclo[5.4.0]undec-7-ene
15 pyrrole
1-methylpyrrole
quinoline
5,6,7,8-tetrahydroisoquinoline
pyrimidine

20 As examples of amines corresponding to the formula (V) there may be mentioned:

N,N'-diethylethylenediamine
N,N-diethyl-N'-methylethylenediamine
N,N'-diethyl-1,3-propanediamine
25 N,N,N',N'-tetramethyl-1,4-butanediamine
N,N,N',N'-tetraethylenediamine

As examples of amines corresponding to the formula (VI) there may be mentioned:

imidazole
30 1-methylimidazole.

Use is advantageously made of a hydrochloride derived from an amine chosen from the group consisting of methylamine, pyridine, methylimidazole, benzylamine, aniline and chloroaniline.

35 A tertiary amine hydrochloride is preferably employed to avoid the risk of amide formation.

The quantity of amine hydrochloride to be used within the scope of the process according to the invention can vary within wide limits.

Good results may be seen with a quantity of amine hydrochloride such that the hydrochloride/Pd molar ratio is between 0.5 and 100 and preferably between 2 and 20.

5 The dicarbonylation reaction may, of course, be used in the absence or in the presence of a solvent exogenic to the reaction system. When it is desired to use organic solvents it is possible to employ polar and basic aprotic solvents such as N-methyl-2-pyrrolidone, 10 tetramethylurea and N,N-dimethylacetamide, or apolar and nonbasic solvents such as esters, saturated aliphatic or cycloaliphatic hydrocarbons or aromatic hydrocarbons.

 When a solvent is used, its quantity represents at least 10 % of the reaction volume; good results can be 15 obtained when of the order of 20 to 90 % by volume is employed.

 The dicarbonylation reaction is generally conducted at a temperature of between 50 and 180°C, preferably between 80 and 150°C, at a carbon monoxide 20 pressure above or equal to 20 bars and preferably below or equal to 250 bar.

 For a good utilization of the process according to the invention the carbon monoxide pressure will be preferably between 90 and 180 bars.

25 Inert gases such as nitrogen, argon or carbon dioxide may be present besides carbon monoxide.

 At the end of the reaction or of the time allocated to the reaction the diacid and/or its diester which is(are) sought after is(are) recovered by any 30 suitable means, for example by extraction and/or distillation.

 The examples below illustrate the invention.

EXAMPLES 1 TO 5; Control test (a):

35 The following are introduced into a 125-cm³ stainless steel (316 L) autoclave purged beforehand with argon:

- 52 mmol of 1,4-dimethoxy-2-butene
- 0.5 mmol of palladium in the form of palladium deposited on active carbon [0.5 g of Pd/C

containing 10 % (wt) of palladium]

- 13.6 mmol of tetrabutylphosphonium chloride
(4 g)

- 5 mmol of the hydrochloride of the amine
5 whose nature is specified in Table I below.

The autoclave is closed hermetically, placed in
an agitated oven and connected to the supply of gas under
pressure. The reactor is purged cold with carbon monoxide
and heated to 120°C. The pressure is then set to 140 bar.
10 After reaction, the autoclave is cooled and degassed.

The reaction mixture is then analysed by gas
phase chromatography.

The particular conditions and the results
obtained appear in Table I below, in which:

15 - t denotes the reaction period at temperature
- H₃D (%) denotes the molar quantity of methyl
3-hexenedioate formed per 100 moles of 1,4-dimethoxy-2-
butene charged, and

- DC (%) denotes the degree of conversion of
20 1,4-dimethoxy-2-butene.

TABLE I

Ref.	Amine from which the hydrochloride is derived	t (h)	DC (%)	H ₃ D (%)
25	1 chloroaniline	2.8	100	73
	2 aniline	2.3	100	69
	3 pyridine	3.5	100	86
	4 methylimidazole	3.0	100	86
30	5 benzylamine	2.4	100	90
	a none	1.5	96	36

Control tests (b) to (d):

35 A series of tests are carried out in the
autoclave and using the operating method described above
on a charge containing:

- 35 mmol of 1,4-dimethoxy-2-butene
- 0.5 mmol of palladium introduced in the form
of palladium deposited on active carbon (10 wt % of

palladium)

- 18.5 mmol of pyridine hydrochloride

No formation of dicarbonylation product is observed at 140 bars and under the particular conditions shown in Table II below:

TABLE II

Ref	T(°C)	t(h)
b	120	0.75
c	140	2
d	150	1

EXAMPLE 6:

A test is carried out in the autoclave and using the operating method described above on a charge containing:

- 34 mmol of 1,2-dimethoxy-3-butene
- 0.5 mmol of palladium in the form of palladium deposited on active carbon [0.5 g of Pd/C containing 10 % (wt) of Pd]]

- 13.6 mmol of tetrabutylphosphonium chloride (4 g)

- 5 mmol of pyridine hydrochloride

After 3 hours' reaction at 120°C and 140 bars the autoclave is cooled and degassed.

The reaction mixture is analysed by high performance liquid chromatography and gas phase chromatography; it is then esterified with methanol at reflux in the presence of traces of sulphuric acid, before being reanalysed by gas phase chromatography.

The results obtained are the following:

- Degree of conversion of dimethoxybutene : 100 %.

Before esterification, the following products are determined (in moles per 100 moles of dimethoxybutene charged) :

- Monomethyl ester of 3-hexene-1,6-dioic acid

= 16 %

- Methyl 3-hexenedioate = 66 %

After esterification, the following is determined:

- Methyl 3-hexenedioate = 77 %

EXAMPLE 7:

5 A test is carried out in the autoclave and using the operating method described above on a charge containing:

- 35 mmol of 1,2-diacetoxy-3-butene
- 0.5 mmol of palladium in the form of palladium deposited on active carbon [0.5 g of Pd/C containing 10 % (wt) of Pd]
- 13.6 mmol of tetrabutylphosphonium chloride (4 g)
- 5 mmol of pyridine hydrochloride

15 After 2.5 hours' reaction at 120°C and 140 bars the autoclave is cooled and degassed.

The reaction mixture is analysed before and after esterification as described in the case of Example 6.

The results obtained are as follows:

- 20 - Degree of conversion of diacetoxybutene : 100 %.

Before esterification, the following products are determined (in moles per 100 moles of diacetoxybutene charged):

- 25 - 3-hexene-1,6-dioic acid = 9 %
- monomethyl ester of 3-hexene-1,6-dioic acid = 24 %
- methyl 3-hexenedioate = 41 %

After esterification, the following is determined :

- 30 - methyl 3-hexenedioate = 66 %

EXAMPLE 8:

A test is carried out in the autoclave and using the operating method described above on a charge containing:

- 35 - 36 mmol of 1,4-diacetoxy-2-butene
- 72 mmol of water
- 0.5 mmol of palladium in the form of palladium deposited on active carbon [0.5 g of Pd/C containing 5 % (wt) of Pd]

- 13.6 mmol of tetrabutylphosphonium chloride

(4 g)

- 5 mmol of pyridine hydrochloride. -

After 3 hours' reaction at 120°C and 140 bar
5 the autoclave is cooled and degassed.

The reaction mixture is analysed before and
after esterification as described in Example 6.

The results obtained are as follows:

- Degree of conversion of diacetoxabutene :

10 100 %

Before esterification:

- 3-hexene-1,6-dioic acid = 47 %

- monomethyl ester of 3-hexene-1,6-dioic acid
= 6 %

15 - methyl 3-hexenedioate = 0 %

After esterification:

- methyl 3-hexenedioate = 48 %

EXAMPLE 9:

A test is carried out in the autoclave and
20 using the operating method described above on a charge
containing:

- 39 mmol of 1,4-butanediol

- 70 mmol of methanol

25 - 0.5 mmol of palladium in the form of
palladium deposited on active carbon [0.5 g of Pd/C
containing 0.5 % (wt) of Pd]

- 13.6 mmol of tetrabutylphosphonium chloride
(4 g)

- 5 mmol of pyridine hydrochloride

30 After 2 hours' reaction at 120°C and 140 bars the
autoclave is cooled and degassed.

The reaction mixture is esterified and then
analysed as described previously.

The results obtained are as follows:

35 - Degree of conversion of 1,4-butanediol =
100 %.

After esterification

- methyl 3-hexenedioate = 50 %

- 3-hexene-1,6-dioic acid = 12 %

EXAMPLES 10 to 15:

A series of tests are carried out in the autoclave and using the operating method described above on a charge containing:

- 5 - 53 mmol of 1,4-dimethoxy-2-butene
- 0.5 mmol of palladium introduced in the form of palladium deposited on active carbon (10 wt %)
- tetrabutylphosphonium chloride in variable quantity, specified in Table III below:
- 10 - 5 mmol of methylamine hydrochloride
- dimethyl adipate: q.s. 50 ml unless stated otherwise.

The particular conditions and the results obtained at 120°C and 140 bar are assembled in Table III below. The conventions employed therein are the same as in the case of Table I.

TABLE III

Ref.	PBu ₄ Cl (mmol)	t (h)	DC %	H3D (%)
10	3.4	4	99.5	52
11	6.8	4	100	70
12	13.6	3	99	72
13	27	4	100	68
14 (*)	6.8	4	100	81
15 (**)	6.8	3	100	60

(*) test carried out with a total volume of 25 cm³ and a water content of 0.2 mmol. The formation of a small quantity (2 %) of the monomethyl ester of 3-hexenedioic acid is observed.

(**) test carried out with a total volume of 25 cm³ and a water content of 6 mmol. The formation of a small quantity (1 %) of the monomethyl ester of 3-hexenedioic acid is observed.

EXAMPLE 16:

A test is carried out in the autoclave and using the operating method described above on a charge containing:

- 35 mmol of 1,4-dimethoxy-2-butene

- 0.5 mmol of palladium introduced in the form
of palladium deposited on active carbon (10 wt %)

- 13.6 mmol of tetrabutylphosphonium chloride

- 5 mmol of pyridine hydrochloride

5 - 10 ml of pentane

The results obtained after 3.3 hours' reaction
at 120°C and 1450 bar are as follows:

- DC (%) = 100

- H3D (%) = 71

10 - monomethyl ester of 3-hexene-1,6-dioic acid
(%) = 24

- 3-hexene-1,6-dioic acid (%) = 3

EXAMPLE 17 to 21:

15 A series of tests are carried out in the
autoclave and using the operating method described above,
on a charge containing:

- 17.8 mmol of 1,2-dimethoxy-3-butene

20 - 0.5 mmol of palladium introduced in the form
of palladium deposited on active carbon containing 10%
(wt) of Pd (unless stated otherwise)

- 14 mmol of tetrabutylphosphonium chloride,

- 2 mmol of hydrochloric acid in aqueous
solution (10 N) (unless stated otherwise)

25 - a hydrocarbon solvent whose nature and
quantity are shown in Table IV below.

At the end of the reaction the reaction mixture
is determined by gas phase chromatography.

30 The particular conditions and the results
obtained at 120°C and 140 bar appear in Table IV below,
in which:

- t(h) denotes the reaction period expressed in
hours:

- H3D (%) at the meaning given above

35 - MME (%) denotes the molar quantity of mono-
methyl ester of 3-hexene-1,6-dioic acid per 100 moles of
1,2-dimethoxy-3-butene charged,

- ACID (%) denotes the molar quantity of 3-
hexene-1,6-dioic acid per 100 moles of 1,2-dimethoxy-3-
butene charged.

TABLE IV

Ref.	Pd mmol	Solvent		t (h)	DC (%)	H3D (%)	MME- (%)	ACID (%)
		nature	ml					
5								
17 (*)	0.5	cyclohexane	30	1	98	14	12	47
18	0.5	"	"	1	100	32	36	27
19	0.5	pentane	60	1.4	94	26	24	33
10	0.2	cyclohexane	30	2	99	40	35	15
21 (**)	0.25	pentane	60	1.7	76	14	12	32

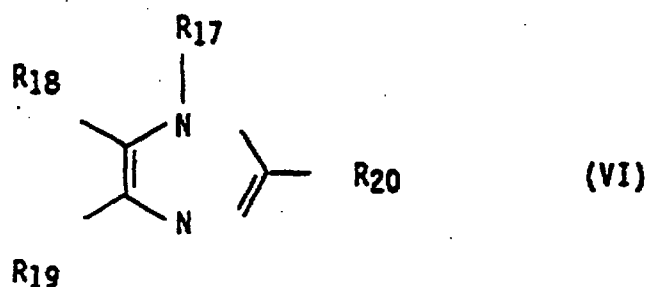
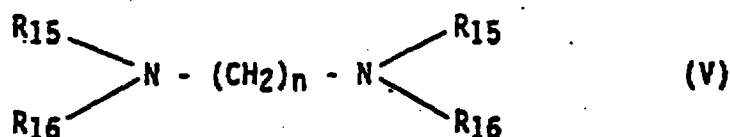
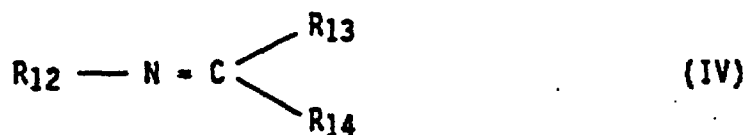
(*) test carried out with 5 mmol of HCl (10 N)

(**) test carried out with 7 mmol of P_{Bu}₄Cl

CLAIMS

1. Process for the linear dicarbonylation of difunctionalized butenes in the liquid phase, at high temperature and at a pressure greater than atmospheric pressure, in the presence of a catalytically effective amount of palladium and of a quaternary onium chloride of an element of group VB chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms, it being possible for the nitrogen to be coordinated to 2 pentavalent phosphorus atoms, characterized in that
 - a) the palladium is charged at least partially in the form of palladium in the zero oxidation state and
 - b) the reaction is also carried out in the presence of at least one hydrogen chloride source.
2. Process according to claim 1, characterized in that the palladium is charged in the form of metallic palladium deposited on a support.
3. Process according to claim 2, characterized in that the support is active charcoal.
4. Process according to any one of the preceding claims, characterized in that the hydrogen chloride source is chosen from the group consisting of gaseous HCl, aqueous HCl solutions, organic HCl solutions and organic chlorides capable of releasing HCl under the reaction conditions.
5. Process according to any one of the preceding claims, characterized in that the hydrochloride derives from an amine corresponding to any one of the formulae (III) to (VI) hereinbelow:





in which:

- R_9 to R_{11} are identical or different and represent:

- a hydrogen atom
- 5 • a linear or branched alkyl radical containing from 1 to 16 carbon atoms and optionally substituted by a phenyl, hydroxyl, halo, nitro, alkoxy or alkoxy carbonyl group;
- 10 • a linear or branched alkenyl radical containing from 2 to 12 carbon atoms
- an aryl radical containing from 6 to 10 carbon atoms and optionally substituted by one or more alkyl, alkoxy, alkoxy carbonyl or halo radicals, the alkyl radicals containing from 1 to 4 carbon atoms;
- 15 • it being possible for two of the said radicals R_9 to R_{11} to form together an alkylene, alkenylene or alkadienylene radical which is linear or branched and which contains from 3 to 6 carbon atoms;



- R_{12} to R_{14} are identical or different and represent:

- a linear or branched alkyl radical containing from 1 to 4 carbon atoms;

5 • it being possible for the radicals R_{13} and R_{14} to form together an alkylene radical containing from 3 to 6 carbon atoms;

10 • it being possible for the radicals R_{12} and R_{13} (or R_{12} and R_{14}) to form together an alkylene, alkenylene or alkadienylene radical containing 4 carbon atoms and constituting, with N, a nitrogenous heterocycle;

- R_{15} and R_{16} are identical or different and represent:

- a hydrogen atom

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

- a linear or branched alkenyl radical containing from 2 to 12 carbon atoms;

- n is an integer between 1 and 6 inclusive;

20 - R_{17} has the meaning given hereinabove for R_1 to R_{11} ;

- R_{18} to R_{20} are identical or different and represent:

- a hydrogen atom;

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

30 • a linear or branched alkenyl radical containing from 2 to 12 carbon atoms.

6. Process according to any one of the preceding claims, characterized in that the amine from which the hydrochloride derives is chosen from the group consisting of methylamine, pyridine, methylimidazole, benzylamine, aniline and chloroaniline.

7. Process according to any one of the preceding claims, characterized in that the hydrochloride derives from a tertiary amine.

8. Process according to any one of the preceding



claims, characterized in that the reaction is carried out in a solvent chosen from the hydrocarbons.

9. Process according to any one of the preceding claims, characterized in that the amine hydrochloride/Pd molar ratio is between 0.5 and 100.
10. Process according to any one of the preceding claims, characterized in that the concentration of the palladium in the reaction medium is between 10^{-3} and 1 mol/l.
- 10 11. Process according to any one of the preceding claims, characterized in that the quaternary onium chloride/Pd molar ratio is between 0.5 and 150 and preferably between 5 and 150.
- 15 12. Process according to any one of the preceding claims, characterized in that the quaternary onium chloride is tetrabutylphosphonium chloride.
13. 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.
- 20 14. 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 15. Process according to any one of the preceding claims, characterized in that the pressure is between 90 and 180 bar.