

5 The present invention relates to a process for the preparation of hexene-1,6-dioic acids. Hexene-1,6-dioic acid is understood more particularly to be hex-3-ene-1,6-dioic acid. Hex-3-ene-1,6-dioic acid can be hydrogenated to adipic acid.

10 Adipic acid, one of the starting materials for nylon 66, is produced in large tonnages and, because of this fact alone, any new access route to this diacid and/or to its derivatives is of immediately apparent interest in principle.

15 More specifically, the subject of the present invention is a process for the preparation of hex-3-ene-1,6-dioic acid by reaction of carbon monoxide and water on at least one butene disubstituted by acyloxy groups in the presence of a catalyst based on palladium.

20 It is indicated in US Patent No. 4,611,082 that the carbonylation of a solution of 1,4-diacetoxy-but-2-ene in a polar and non-basic aprotic solvent, chosen from the group comprising the nitriles, bis(2-methoxy)but-2-ene, bis(2-methoxyethyl) ether and methylene chloride, at 80-140°C in the presence of a transition metal halide is virtually not observed and that in the presence of an alcohol the rates increase and are comparable to those found for the carbonylation of but-2-ene-1,4-diol. With
25 regard to this last-men-tioned substrate, it is also indicated that it is not possible to achieve satisfactory yields of straight-chain carbonylation products under the abovementioned conditions and, in this context, preference is given to the substrates substituted in the 1,4-position
30 by alkoxy groups.

In this context, it would therefore appear that 1,4-diacetoxy-but-2-ene cannot be regarded as a promising substrate for forming dicarbonylated straight-chain products.

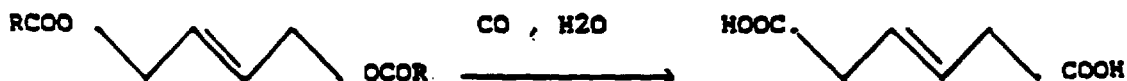
35 However, 1,4-diacetoxy-but-2-ene is readily accessible by acetoxylation of butadiene. It would therefore be highly desirable to be able to have available a process enabling dicarbonylated straight-chain products to be obtained with a high efficiency from 1,4-diacetoxy-

but-2-ene, for example, and more generally from butenes disubstituted by acyloxy groups.

The subject of the present invention is therefore a process for the preparation of hexene-1,6-dioic acids by reaction of carbon monoxide and water on at least one butene disubstituted by acyloxy groups in the presence of a catalyst based on palladium and of a quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms and it being possible for nitrogen to be coordinated to two pentavalent phosphorus atoms.

In fact, it has been found, in a wholly surprising manner, that a process of this type enables the dicarbonylation to be carried out under pressure and temperature conditions acceptable on an industrial scale, with an appreciable selectivity for the straight-chain dicarbonylated product.

The process in question can be represented by the following reaction scheme, when the starting material is a but-2-ene disubstituted in the 1,4-position by acyloxy groups,



in which R represents:

- . a straight-chain or branched alkyl radical containing 1 to 12 carbon atoms, optionally substituted by a phenyl group;
 - or . an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or two alkyl radicals containing 1 to 4 carbon atoms;
- and can carry 1 to 3 substituents chosen from fluorine and chlorine atoms and dialkylamino and N,N-dialkylamido groups in which the alkyl radicals contain at most 4 carbon atoms.

The process according to the present invention requires the use of at least one butene disubstituted by acyloxy groups. Acyloxy group is understood to be groups of formula RCOO- in which R has the meaning given above;

disubstituted butenes are understood to be the compounds of but-2-ene substituted in the 1 and 4 positions and the compounds of but-1-ene substituted in the 3 and 4 positions. Of course, mixtures of but-2-ene disubstituted by
5 acyloxy groups of different nature, mixtures of but-1-ene disubstituted by acyloxy groups of different nature or mixtures of disubstituted but-2-ene and but-1-ene can be used within the framework of the present process.

In fact, it has been found by the Applicant that the
10 selectivity for straight-chain acid is substantially the same whether a but-2-ene disubstituted by acyloxy groups in the 1,4-positions or a but-1-ene disubstituted by acyloxy groups in the 3 and 4 positions is used as the starting material.

15 The following may be mentioned as examples of butenes disubstituted by acyloxy groups: diacetoxymutenes, di-propionyloxybutenes, dibutyryloxybutenes and dibenzoyloxybutenes.

1,4-Diacetoxymuten-2-ene, 3,4-diacetoxymuten-1-ene and
20 their mixtures are very particularly suitable for carrying out the present invention.

The process according to the present invention also requires the presence of water.

The amount of water to be used within the framework
25 of the present process is not critical and can vary within wide limits.

For a good implementation of the reaction, the molar ratio of water to disubstituted butene will be between 1 and 100 and preferably between 1 and 50.

30 The process according to the present invention is carried out in the presence of a catalyst based on palladium.

Although the precise nature of the one or more catalytically active species in the reaction in question
35 may not be totally elucidated, the Applicant has found that diverse palladium compounds and metallic palladium are capable of being useful precursors in carrying out the present process.

The following may be mentioned amongst the sources of

palladium which can be used for carrying out the process which is the subject of the invention:

. metallic palladium, where appropriate deposited on a carrier, such as carbon, alumina or silica,

5 . PdCl_2 , $\text{Pd}(\text{OAc})_2$, PBu_4PdCl , ($\text{Bu} = n\text{-butyl}$)

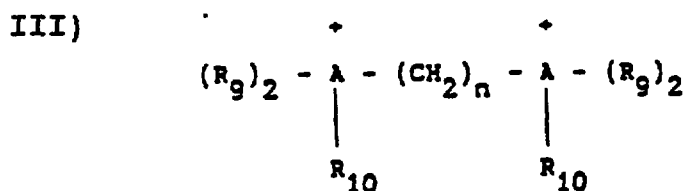
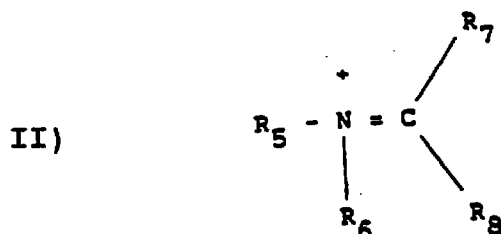
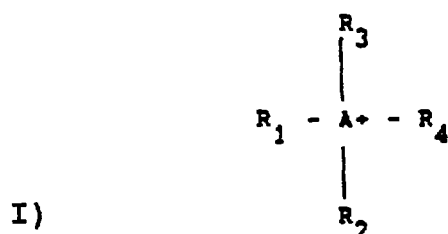
. the salts or π -allyl complexes of palladium, in which the anion coordinated to the Pd cation is chosen from the following anions: carboxylates such as formate, acetate, propionate and benzoate; acetylacetonate and
10 halides such as Cl^- and Br^- , and preferably Cl^- ;

The precise amount of catalyst to be used, which can vary within wide limits, will above all depend on a compromise between the desired efficiency and the consumption of catalyst and on other conditions chosen for
15 the reaction. In general, good results can be obtained with a palladium concentration in the reaction mixture of between 10^{-3} and 1 mol/l. Preferably, this concentration is between $2 \cdot 10^{-3}$ and $5 \cdot 10^{-2}$ mol/l.

One of the essential characteristics of the present
20 process lies in the fact that the reaction is also carried out in the presence of a quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to the carbon atoms and it also being possible for nitrogen to be coordinated
25 to two pentavalent phosphorus atoms.

Quaternary onium cation in which the group VB element is tetracoordinated to the carbon atoms is understood to be cations formed from nitrogen or phosphorus and four monovalent, identical or different, hydrocarbon groups, in
30 which the free valency is carried by a carbon atom, each group being bonded to the abovementioned element by the said free valency and any two of these groups, moreover, being able to form together a divalent radical.

For a good implementation of the process of the
35 invention, the quaternary onium chloride has a quaternary onium cation corresponding to one of the formulae I to IV below:



IV)



5 in which formulae:

- A represents nitrogen or phosphorus

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

10 . a straight-chain or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halogeno, nitro, alkoxy or alkoxy-carbonyl group;

15 . a straight-chain 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 radicals containing 1 to 4 carbon atoms, alkoxy, alkoxy-carbonyl or halogeno;

20 . it being possible for two of the said radicals R_1

to R_4 to form together a straight-chain or branched alkylene, alkenylene or alkadienylene radical containing 3 to 6 carbon atoms;

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

 . a straight-chain or branched alkyl radical containing 1 to 4 carbon atoms; -

 . it being possible for the radicals R_7 and R_8 to form together an alkylene radical containing 3 to 6 carbon atoms;

10 . 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, with N, a nitrogen-containing heterocyclic radical;

15 - R_9 represents a straight-chain or branched alkyl radical containing 1 to 4 carbon atoms or a phenyl radical;

 - R_{10} represents:

20 . a straight-chain or branched alkyl radical containing 1 to 4 carbon atoms, similar to or different from R_9 ;

 . a straight-chain or branched alkenyl radical containing 2 to 12 carbon atoms, preferably 4 to 8 carbon atoms;

25 - 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;

30 - R_{11} represents an aryl radical containing 6 to 10 carbon atoms, optionally substituted by one or more alkyl groups containing 1 to 4 carbon atoms, alkoxy, alkoxy-carbonyl or halogeno.

The following cations may be mentioned as examples of quaternary onium cations corresponding to formula I:

- 35 . tetramethylammonium
 . triethylmethylammonium
 . tributylmethylammonium
 . trimethyl(n-propyl)ammonium
 . tetraethylammonium
 . tetrabutylammonium

- . dodecyltrimethylammonium
- . methyltrioctylammonium
- . heptyltributylammonium
- . tetrapropylammonium
- 5 . tetrapentylammonium
- . tetrahexylammonium
- . tetraheptylammonium
- . tetraoctylammonium
- . tetradecylammonium
- 10 . butyltripropylammonium
- . methyltributylammonium
- . pentyltributylammonium
- . methyldiethylpropylammonium
- . ethyldimethylpropylammonium
- 15 . tetradodecylammonium
- . tetraoctadecylammonium
- . hexadecyltrimethylammonium
- . benzyltrimethylammonium
- . benzyl dimethylpropylammonium
- 20 . benzyl dimethyloctylammonium
- . benzyltributylammonium
- . benzyltriethylammonium
- . phenyltrimethylammonium
- . benzyl dimethyltetradecylammonium
- 25 . benzyl dimethylhexadecylammonium
- . dimethyldiphenylammonium
- . methyltriphenylammonium
- . but-2-enyltriethylammonium
- . N,N-dimethyltetramethyleneammonium
- 30 . N,N-diethyltetramethyleneammonium
- . tetramethylphosphonium
- . tetrabutylphosphonium
- . ethyltrimethylphosphonium
- . trimethylpentylphosphonium
- 35 . octyltrimethylphosphonium
- . dodecyltrimethylphosphonium
- . trimethylphenylphosphonium
- . diethyldimethylphosphonium
- . dicyclohexyldimethylphosphonium

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

30 The following cations may be mentioned amongst the cations corresponding to formula II:

- . N-methylpyridinium
- . N-ethylpyridinium
- . N-hexadecylpyridinium
- . N-methylpicolinium

35 The following cations may be mentioned amongst the cations corresponding to formula III:

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

. 1,3-bis(trimethylammonium)butane

The following cations may be mentioned amongst the cations corresponding to formula IV:

bis(triphenylphosphine)iminium

5 bis(tritolylphosphine)iminium.

Advantageously, the cations used are those onium cations corresponding to formula (I) above in which:

- A represents phosphorus, and

10 - R_1 , R_2 , R_3 and R_4 are identical or different and represent a straight-chain or branched alkyl radical containing 1 to 8 carbon atoms or a phenyl or 4-methylphenyl radical.

A tetraalkylphosphonium chloride is preferably used.

15 Tetrabutylphosphonium chloride, which is available and particularly efficient, is very particularly recommended.

It will be noted that certain palladium compounds, such as PBu_4PdCl_3 , which has been mentioned above and results from the reaction between equivalent molar amounts of PBu_4Cl and $PdCl_2$, can at one and the same time constitute a source of palladium and a means of introducing a quaternary onium chloride in the sense indicated above.

25 It has been found that the beneficial effect afforded by the presence in the carbonylation mixture of a quaternary onium chloride corresponding to the definition given above is perceptible from an onium cation/palladium molar ratio of 0.5; notably a particularly worthwhile effect has been found when the said ratio is between 1 and 50, it even being possible to choose a higher ratio without prejudice to the reaction. In fact, the quaternary onium chloride can be used in a relatively significant amount and, so to speak, play the supplementary role of a diluent for the reaction mixture.

35 It will generally be possible to carry out the reaction in liquid phase at a temperature of between 50 and 150°C, preferably between 80 and 130°C, under a carbon monoxide pressure of between 10 and 250 bar (1000 and 25,000 kPa), preferably between 15 and 180 bar (1500 and 18,000 kPa).

Inert gases, such as nitrogen, argon or carbon dioxide, can be present alongside the carbon monoxide.

Of course, the reaction can be carried out in the presence of solvents or diluents exogenous to the reaction mixture, such as aromatic hydrocarbons, esters, ketones,
5 nitriles or carboxylic acid amides.

According to an advantageous variant of the process according to the present invention, the reaction is carried out in N-methylpyrrolidone.

10 The concentration of disubstituted butene can vary within wide limits.

At the end of the reaction or of the desired reaction time, the desired diacid is recovered by any appropriate means, for example by extration.

15 The examples which follow illustrate the invention.

In these examples, the degree of conversion is 100 % and the formation of the various acids below is observed:

- HD : mixture of hex-3-enedioic and hex-2-enedioic acids in which hex-3-enedioic acid is
20 predominant.
- Ac.C₅ : mixture of valeric, 2-methylbutyric, pent-3-enoic, pent-2-enoic and pent-4-enoic acids in which pent-3-enoic acid is pre-
dominant.
- 25 - C₆sat. : mixture of ethylsuccinic, methylglutaric and adipic acids in which methylglutaric acid is predominant.
- PDO : pentadienoic acid

the number of moles formed per 100 moles of diacetoxy-
30 butene charged being indicated for each group.

EXAMPLES 1 TO 11; Reference experiments (a) and (b):

The following are introduced into a 125 cm³ stainless steel (Hastelloy B2) autoclave previously purged with argon:

- 35 - 8.6 g (50 mmol) of 1,4-diacetoxybut-2-ene
- 1.8 g (100 mmol) of water
- 1 mg-at. of palladium in the form indicated in Table I below:
- 5 g (17 mmol) of PBu₄Cl

- 25 cm³ of solvent, the nature of which is given in Table I below:

5 The autoclave is hermetically sealed, placed in an agitated furnace and adjusted to feeding with gas under pressure. The reactor is purged cold with carbon monoxide and brought to 100°C. The pressure is then adjusted to 120 bar. After a reaction time of 6 hours (unless indicated otherwise), the autoclave is cooled and degassed.

10 The resultant reaction mixture is diluted to 100 cm³ with the solvent.

An aliquot portion is esterified with methanol and then analysed by gas phase chromatography.

TABLE I

				Results (%)			
Ex. No.	Pd	Solvent	t(h)	HD	Ac.C ₅	C ₆ sat.	PDO
5	1	PdCl ₂		34	35	17	0
	(a)	"		6	16	5	4
	(b)	"		2	33	11	1
10	2	Pd(OAc) ₂	2	38	2	1	15
	3*	id+HBF ₄		22	32	17	0
	4	PdCl ₂	3	68	2	0	12
	5	Pd(OAc) ₂		22	1	0	41
	6	Pd(dba) ₂		20	0.5	0	40
	7	MePO ₃ PdCl ₃		60	1	0	12
15	8*	Pd/C		17	3	-	54
	9	PdCl ₂	3	80	4	1	1
	10	"		33	0	0	11
	11	"		38	20	0	0.5

(a) : PBu₄Cl absent

(b) : PBu₄Cl replaced by PBu₄Br

20 3 (*) catalyst: Pd(OAc)₂ + 2mmol HBF₄

8 (*) catalyst: Pd/C (10 % palladium); 1 mmol Pd.

t(h) : absorption time if it is less than 6 hours.

EXAMPLE 12:

25 Example 4 above is repeated using only 0.5 mg-at. of palladium in the form of PdCl₂. The following results are obtained in a reaction time of 12 hours:

- HD : 80 %

- Ac.C₅ : 0.5 %

- C₆sat. : 0 %

30 - PDO : 14 %

EXAMPLE 13:

Example 4 above is repeated using only 0.25 mg-at. of palladium in the form of PdCl₂. The following results are obtained in a reaction time of 12 hours:

- HD : 65 %
 - Ac.C₅ : 2 %
 - C₆sat. : 0 %
 - PDO : 12 %

5 EXAMPLES 14 AND 15:

Example 4 above is repeated using, respectively, 2.5 g and 15 g of PBU₄Cl and adjusting the volume of N-methylpyrrolidone for each experiment in such a way that the total volume of the charge is constant.

10 The results obtained are indicated in Table II below, in which the results and particular conditions of Examples 4 and 9 above are repeated.

TABLE II

Ex. No.	PBU ₄ Cl(g)	t(h)	Results (%)			
			HD	Ac.C ₅	C ₆ sat.	PDO
14	2.5	6	55	1	0	13
4	5	3	68	2	0	12
15	15	3	80	3	0	3
9	30	3	78	4	1	1

20 EXAMPLE 16:

Example 4 above is repeated replacing the 1,4-diacetoxybut-2-ene in the charge by an equivalent amount of 1,2-diacetoxybut-3-ene.

25 After a reaction time of 6 hours, the results obtained are as follows:

- HD : 65 %
 - Ac.C₅ : 1 %
 - C₆sat. : 0 %
 - PDO : 10 %

30 EXAMPLE 17:

Example 4 above is repeated at 130°C.

After a reaction time of 3 hours, the results obtained are as follows:

35 - HD : 45 %
 - Ac.C₅ : 7 %

- C₆sat. : 0 %
- PDO : 0 %

EXAMPLE 18:

Example 4 above is repeated at 70°C.

5 After a reaction time of 6 hours, the results obtained are as follows:

- HD : 30 %
- Ac.C₆ : 2 %
- C₆sat. : 0 %
10 - PDO : 33 %

EXAMPLE 19:

Example 4 above is repeated under a pressure of 180 bars.

Approximately the same results are obtained.

15 EXAMPLE 20:

Example 4 above is repeated under a pressure of 15 bars.

After a reaction time of 6 hours, the results obtained are as follows:

20 - HD : 40 %
- Ac.C₆ : 30 %
- C₆sat. : 0 %
- PDO : 2 %

EXAMPLE 21:

25 Example 4 above is repeated under a pressure of 60 bars.

After a reaction time of 6 hours, the results obtained are as follows:

30 - HD : 75 %
- Ac.C₆ : 3 %
- C₆sat. : 0 %
- PDO : 9 %

EXAMPLES 22 TO 24:

35 Example 4 above is repeated twice using, respectively, 25 mmol and 100 mmol of 1,4-diacetoxybut-2-ene (DAB), in each experiment maintaining a 1,4-diacetoxybut-2-ene/H₂O molar ratio of 1/2 and keeping the volume of the charge constant by adjusting the amount of NMP (Examples 22 and 23).

Example 1 above is repeated using 25 mmol of 1,4-diacetoxybut-2-ene, maintaining the molar ratio of the latter with water at 1/2 and keeping the volume of the charge constant by adjusting the amount of CH₃CN (Example 24).

The results obtained are given in Table III below:

TABLE III

Ex. No.	Solvent	DAB mmol	t(h)	Results (%)			
				HD	Ac.C ₂	C ₂ sat.	PDO
22	NMP	25	3	80	1	?	7
4	"	50	3	68	2	0	12
23	"	100		60	2	0	15
24	CH ₃ CN	25		68	23	22	0
1	"	50		45	35	17	0

t(h): absorption time if it is less than 6 hours

EXAMPLES 25 AND 26:

Example 1 above is repeated varying the amount of water charged.

The particular conditions and the results obtained are given in Table IV below:

TABLE IV

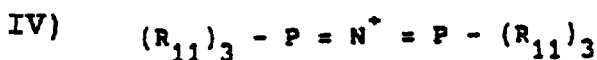
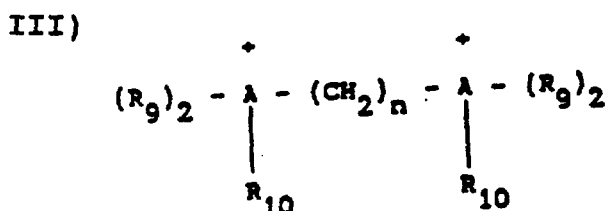
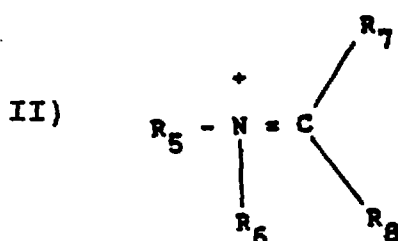
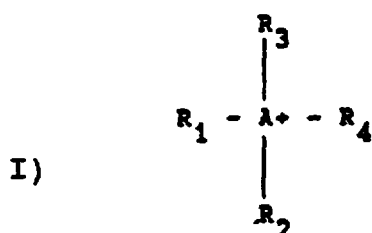
Ex. No.	H ₂ O mmol	t(h)	Results (%)			
			HD	Ac.C ₂	C ₂ sat	PDO
1	100	6	45	35	17	0
25	200	2.5	48	27	9	0
26	500	3	45	4	5	5



CLAIMS

1. Process for the preparation of hexene-1,6-dioic acids by reaction of carbon monoxide and water on at least one butene disubstituted by acyloxy groups in the presence of a catalyst based on palladium and at least one quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus, the said element being tetracoordinated to carbon atoms and it being possible for nitrogen to be coordinated to two pentavalent phosphorus atoms.

2. Process according to claim 1, characterized in that the quaternary onium chloride of a group VB element chosen from nitrogen and phosphorus has a quaternary onium cation corresponding to one of the formulae (I) to (IV) below:



in which formulae:

- A represents nitrogen or phosphorus
- R_1 , R_2 , R_3 and R_4 are identical or different and represent:



. a straight-chain or branched alkyl radical containing 1 to 16 carbon atoms, optionally substituted by a phenyl, hydroxyl, halogeno, nitro, alkoxy or alkoxy-carbonyl group;

. a straight-chain 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 radicals containing 1 to 4 carbon atoms, alkoxy, alkoxy-carbonyl or halogeno;

. it being possible for two of the said radicals R_1 to R_4 to form together a straight-chain 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:

. a straight-chain or branched alkyl radical containing 1 to 4 carbon atoms;

. it being possible for the radicals R_7 and R_8 to form together an alkylene radical containing 3 to 6 carbon atoms;

. 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, with N, a nitrogen-containing heterocyclic radical;

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

- R_{10} represents:

. a straight-chain or branched alkyl radical containing 1 to 4 carbon atoms, similar to or different from R_9 ;

. a straight-chain 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 groups containing 1 to 4 carbon atoms, alkoxy, alkoxy carbonyl or halogeno.

3. Process according to claim 1 or 2, characterized in that the quaternary onium cation corresponds to the formula (I) given in claim 2, in which:

- A represents phosphorus, and

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

4. Process according to any one of the preceding claims, characterized in that the quaternary onium chloride is tetrabutylphosphonium chloride.

5. Process according to any one of the preceding claims, characterized in that the molar ratio of the onium cation to palladium is greater than or equal to 1.

6. Process according to any one of the preceding claims, characterized in that the concentration of palladium in the reaction mixture is between 10^{-3} and 1 mol/l.

7. Process according to any one of the preceding claims, characterized in that the molar ratio of water to disubstituted butene is between 1 and 100 and preferably between 1 and 50.

8. Process according to any one of the preceding claims, characterized in that the reaction temperature is between 50 and 150°C and preferably between 80 and 130°C.

9. Process according to any one of the preceding claims, characterized in that the pressure is between 10 and 250 bar (1000 and 25,000 kPa) and preferably between 15 and 180 bar (1500 and 18,000 kPa).

10. Process according to any one of the preceding claims, characterized in that the disubstituted butene is chosen from 1,4-diacetoxybut-2-ene and 3,4-diacetoxybut-1-ene and their mixtures.

11. Process according to any one of the preceding



claims, characterized in that the reaction is carried out in the presence of an organic solvent or diluent.

12. Process according to claim 11, characterized in that the solvent is N-methylpyrrolidone.