

The present invention relates to a process for preparing β,γ -unsaturated acids. It relates more especially to a process for preparing β,γ -unsaturated acids by the carbonylation of allyl alcohols.

5 In US Patent No. 4,189,608, a process is described for preparing 3-butenic acid by bringing allyl alcohol and carbon monoxide into contact in the presence of a palladium chloride-based catalyst at a temperature of 50 to 300°C under high pressure, the reaction being
10 performed in a substantially anhydrous C_2 - C_{10} carboxylic acid as a liquid solvent.

In point of fact, the carboxylic acid is liable to react with the alcohol to give rise to an allyl carboxylate, which would become the reactant for the
15 palladium-catalysed carbonylation.

Moreover, the catalytic activity remains low, as evidenced by the relatively long reaction times.

In US Patent No. 4,025,547, a description is given of the carbonylation of primary allyl alcohols to
20 esters of the allyl vinylacetate type in the presence of a homogeneous catalytic system containing three components:

- a palladium halide with
- one or more donor ligands of group VB, and
- 25 - a cocatalyst which is a halide of a group IVB metal.

A typical example of these catalytic compositions is $PdCl_2(P(C_6H_5)_3)_2 \cdot SnCl_2$.

Triphenylphosphine as well as tin dichloride may
30 be introduced in excess.

In this process, an allyl ester is formed instead of an acid; the allyl alcohol acts both as a substrate which is carbonylated under the reaction conditions and as an esterification reagent. Moreover, the pressures
35 employed are very high.

In German Offenlegungsschrift 3,345,375, a process is described for the carbonylation of secondary or

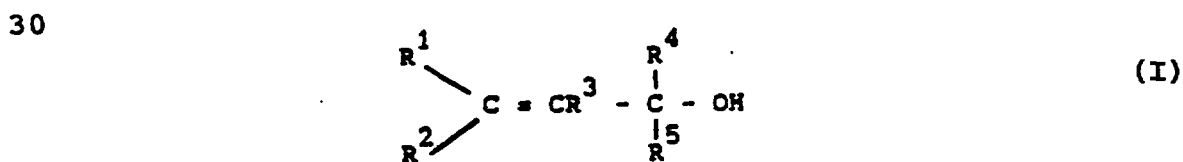
tertiary allyl alkanols in the presence of palladium halides complexed with a phosphine, where appropriate in excess, at 50-150°C under high pressure.

While the selectivity of the reaction appears to be appreciable, the activity of the catalytic system remains low, as evidenced both by the long reaction times and the very high pressures which are employed in this process.

It has now been found possible to obtain β,γ -unsaturated acids by the carbonylation of allyl alcohols with an improved efficiency, in particular under milder pressure conditions than those required hitherto.

The subject of the present invention is hence a process for preparing β,γ -unsaturated acids by bringing an allyl alcohol, carbon monoxide and a palladium-based catalyst into contact at high temperature and under a pressure above atmospheric pressure, characterized in that the reaction is also performed in the presence of at least one quaternary onium chloride of a group VB element selected from nitrogen and phosphorus, the said element being four-coordinated to carbon atoms, it being possible for the nitrogen to be coordinated to two pentavalent phosphorus atoms.

In the context of the process according to the present invention, allyl alcohol is understood to mean an unsaturated mono- or dihydroxylated compound corresponding to the general formula:



35 in which:

R^1 to R^5 , which may be identical or different, represent:

- a hydrogen atom,
 - an alkyl, aryl or aralkyl radical containing at most 20 carbon atoms,
 - an alkenyl radical free from terminal unsaturation and containing at most 15 carbon atoms,
- 5
- . any one of the radicals R^1 to R^5 can, in addition, represent a hydroxymethyl radical ($-\text{CH}_2\text{OH}$),
- 10
- . R^1 (or R^2) and R^4 (or R^5) together can, in addition, form a single divalent alkylene radical containing from 2 to 5 carbon atoms.

When one of the radicals R^1 to R^5 represents a hydroxymethyl radical, all the other radicals R^1 to R^5 preferably represent a hydrogen atom.

15

The hydroxymethyl group is reactive under the conditions of the present process, and it has also been found, quite surprisingly, that it is possible to obtain 3-hexene-1,6-dioic acid with appreciable selectivity from 2-butene-1,4-diol as well as from 1-butene-3,4-diol or mixtures thereof. It should be noted that hexene-1,6-dioic acid may be hydrogenated to adipic acid.

20

Adipic acid, one of the raw materials of nylon 66, is produced in vast tonnages and, for this reason alone, any new access route to this diacid and/or its derivatives, is theoretically of immediately obvious interest.

25

As is apparent on reading the general formula (I) above, primary, secondary or tertiary allyl alcohols are capable of being employed in the context of the present process.

30

By way of examples of such alcohols, the following may be mentioned:

- 35
- allyl alcohol
 - 2-buten-1-ol (crotyl alcohol)
 - 3-buten-2-ol (1-methylallyl alcohol)

- 1-penten-3-ol
- 1-hexen-3-ol
- 1-octen-3-ol
- 3,7-dimethyl-2,6-octadien-1-ol (geraniol)
- 5 3,7-dimethyl-1,6-octadien-3-ol (linalool)
- 3-phenyl-2-propen-1-ol (cinnamyl alcohol)
- 2-methyl-1-propen-3-ol
- 2-cyclohexen-1-ol
- 3-methyl-1-buten-3-ol
- 10 2-butene-1,4-diol
- 1-butene-3,4-diol

The process according to the present invention is performed in the presence of a palladium-based catalyst.

- 15 Although the exact nature of the species (one or more) which is/are catalytically active in the reaction in question has not been completely elucidated, the Applicant has observed that various palladium compounds and palladium metal are capable of being useful
- 20 precursors in the implementation of the present process.

- Among sources of palladium capable of being employed for carrying out the process which forms the subject of the invention, the following may be
- 25 mentioned:

- . palladium metal deposited, where appropriate, on a support such as charcoal, alumina or silica,
- . PdCl_2 , $\text{Pd}(\text{OAc})_2$, PBu_4PdCl , (Bu = n-butyl)
- . salts or π -allyl complexes of palladium in which
- 30 the anion coordinated to the Pd cation is selected from the following anions: carboxylates such as formate, acetate, propionate, benzoate; acetylacetonate, halides such as Cl^- and Br^- , and preferably Cl^- .

- The exact quantity of catalyst to be employed,
- 35 which can vary within wide limits, will depend above all on a compromise between the desired efficiency and the outlay on the catalyst, and on the other conditions

selected for the reaction.

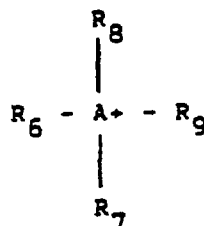
In general, good results may be obtained with a concentration of palladium in the reaction medium of between 10^{-3} and 1 mol/l. Preferably, this concentration is between 2×10^{-3} and 5×10^{-2} Mol/l.

One of the essential features of the present process lies in the fact that the reaction is also performed in the presence of a quaternary onium chloride of a group VB element selected from nitrogen and phosphorus, the said element being four-coordinated to carbon atoms, it being possible for the nitrogen in addition to be coordinated to pentavalent phosphorus atoms.

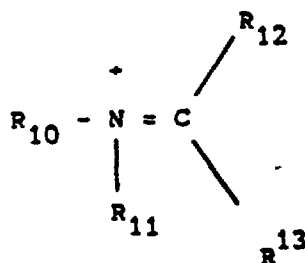
Quaternary onium cation in which the group VB element is four-coordinated to carbon atoms is understood to mean cations formed from nitrogen or phosphorus and from four identical or different monovalent hydrocarbon groups, the free valency of which is carried by a carbon atom, each group being attached to the abovementioned element via the said free valency, it being possible, moreover, for any two of these groups together to form a divalent radical.

For good implementation of the process of the invention, the quaternary onium chloride possesses a quaternary onium cation corresponding to one of the formulae II to V below:

II)

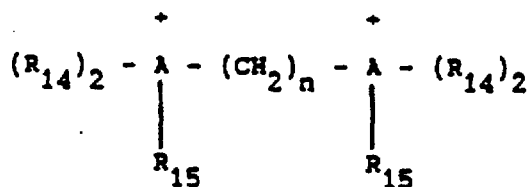


III)



iv)

6



5

v)



in which:

10

- A represents nitrogen or phosphorus;

- R_6 , R_7 , R_8 and R_9 are identical or different and represent:

15

. a linear or branched alkyl radical containing from 1 to 16 carbon atoms, optionally substituted with a phenyl, hydroxy, halo, nitro, alkoxy or alkoxy-carbonyl group;

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

20

. an aryl radical containing from 6 to 10 carbon atoms, optionally substituted with one or more alkyl radicals containing from 1 to 4 carbon atoms, or alkoxy, alkoxycarbonyl or halo radicals;

25

. it being possible for two of the said radicals R_6 to R_9 together to form a linear or branched alkylene, alkenylene or alkadienylene radical containing from 3 to 6 carbon atoms;

- R_{10} , R_{11} , R_{12} and R_{13} are identical or different and represent:

30

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

. it being possible for the radicals R_{12} and R_{13} together to form an alkylene radical containing from 3 to 6 carbon atoms;

35

. it being possible for the radicals R_{11} and R_{12} or R_{11} and R_{13} together to form an alkylene, alkenylene or alkadienylene radical containing 4 carbon atoms and

constituting with N a nitrogenous heterocycle;

- R_{14} represents a linear or branched alkyl radical containing from 1 to 4 carbon atoms or a phenyl radical;

5 - R_{15} represents:

 . a linear or branched alkyl radical containing from 1 to 4 carbon atoms, similar to or different from R_{14} ;

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

 - n represents an integer not less than 1 and not more than 10, and preferably not more than 6;

15 - R_{16} represents an aryl radical containing from 6 to 10 carbon atoms, optionally substituted with one or more alkyl groups containing from 1 to 4 carbon atoms, or alkoxy, alkoxycarbonyl or halo groups.

20 By way of example of quaternary onium cations corresponding to the formula II, the following cations may be mentioned:

 tetramethylammonium

 triethylmethylammonium

 tributylmethylammonium

 trimethyl(n-propyl)ammonium

25 tetraethylammonium

 tetrabutylammonium

 dodecyltrimethylammonium

 methyltrioctylammonium

 heptyltributylammonium

30 tetrapropylammonium

 tetrapentylammonium

 tetrahexylammonium

 tetraheptylammonium

 tetraoctylammonium

35 tetradecylammonium

 butyltripropylammonium

 methyltributylammonium

	pentyltributylammonium
	methyldiethylpropylammonium
	ethyldimethylpropylammonium
	tetradodecylammonium
5	tetraoctadecylammonium
	hexadecyltrimethylammonium
	benzyltrimethylammonium
	benzyldimethylpropylammonium
	benzyldimethyloctylammonium
10	benzyltributylammonium
	benzyltriethylammonium
	phenyltrimethylammonium
	benzyldimethyltetradecylammonium
	benzyldimethylhexadecylammonium
15	dimethyldiphenylammonium
	methyltriphenylammonium
	(2-butenyl)triethylammonium
	N,N-dimethyl(tetramethylen)ammonium
	N,N-diethyl(tetramethylen)ammonium
20	tetramethylphosphonium
	tetrabutylphosphonium
	ethyltrimethylphosphonium
	trimethylpentylphosphonium
	octyltrimethylphosphonium
25	dodecyltrimethylphosphonium
	trimethylphenylphosphonium
	diethyldimethylphosphonium
	dicyclohexyldimethylphosphonium
	dimethyldiphenylphosphonium
30	cyclohexyltrimethylphosphonium
	triethylmethylphosphonium
	methyltri(isopropyl)phosphonium
	methyltri(n-propyl)phosphonium
	methyltri(n-butyl)phosphonium
35	methyltri(2-methylpropyl)phosphonium
	methyltricyclohexylphosphonium
	methyltriphenylphosphonium

- methyltribenzylphosphonium
 methyltri(4-methylphenyl)phosphonium
 methyltrixylylphosphonium
 diethylmethylphenylphosphonium
 5 dibenzylmethylphenylphosphonium
 ethyltriphenylphosphonium
 tetraethylphosphonium
 ethyltri(n-propyl)phosphonium
 triethylpentylphosphonium
 10 hexadecyltributylphosphonium
 ethyltriphenylphosphonium
 n-butyltri(n-propyl)phosphonium
 butyltriphenylphosphonium
 benzyltriphenylphosphonium
 15 (β -phenylethyl)dimethylphenylphosphonium
 tetraphenylphosphonium
 triphenyl(4-methylphenyl)phosphonium
 tetrakis(hydroxymethyl)phosphonium
 tetrakis(2-hydroxyethyl)phosphonium
 20 Among cations corresponding to the formula III,
 the following cations may be mentioned:
 N-methylpyridinium
 N-ethylpyridinium
 N-hexadecylpyridinium
 25 N-methylpicolinium
 Among cations corresponding to the formula IV, the
 following cations may be mentioned:
 1,2-bis(trimethylammonium)ethane
 1,3-bis(trimethylammonium)propane
 30 1,4-bis(trimethylammonium)butane
 1,3-bis(trimethylammonium)butane
 Among cations corresponding to the formula V, the
 following cations may be mentioned:
 bis(triphenylphosphine)iminium
 35 bis(tritolylphosphine)iminium.
 Use is advantageously made of those onium cations
 corresponding to the formula (II) above in which:

- A represents phosphorus, and
- R_6 , R_7 , R_8 and R_9 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.

5

A tetraalkylphosphonium chloride is preferably used.

Tetrabutylphosphonium chloride, which is available and particularly efficient, is more especially recommended.

10

It will be noted that some palladium compounds, such as PBu_4PdCl , mentioned above and resulting from the reaction between equivalent molar quantities of PBu_4Cl and PdCl_2 , can constitute both a source of palladium and a means of introduction of a quaternary onium chloride within the meaning stated above.

15

It has been found that the beneficial effect provided by the presence in the carbonylation medium of a quaternary onium chloride corresponding to the definition given above is substantial at and above an onium cation/palladium mole ratio of 0.5; in particular, an especially advantageous effect has been observed when the said ratio is between 1 and 50, it even being possible for a higher ratio to be selected without detriment to the reaction. In effect, the quaternary onium chloride may be used in relatively large quantities and play, as it were, the additional part of a diluent of the reaction medium.

20

25

The reaction may be generally performed in the liquid phase at a temperature of between 50 and 150°C, and preferably between 80 and 130°C, under a carbon monoxide pressure of between 10 and 250 bars (1,000 and 25,000 KPa), and preferably between 15 and 180 bars (1,500 and 18,000 KPa).

30

35

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

Naturally, the reaction may be performed in the

presence of solvents or diluents exogenous to the reaction medium, such as esters, ketones, nitriles, aromatic hydrocarbons, dimethyl sulphoxide or carboxylic acid amides.

5 The presence of water, even in relatively large quantities (of the order of 10 moles per mole of substrate), is not detrimental and is capable, under certain conditions, of having a beneficial effect on the selectivity or even the activity.

10 The presence of a lower alkanol can prove desirable in some cases. In effect, although such an alcohol cannot be considered to be inert under the reaction conditions, it may be introduced as a coreagent for esterifying the β,γ -[lacuna] acid formed,
15 and this can constitute an alternative for, for example, isolating the desired product more conveniently in its ester form. This ester may then be hydrolysed in a manner known per se to recover the desired product in its acid form.

20 This variant can be more especially advantageous when the allyl alcohol involved in the reaction is a a butenediol and when the alkanol used is methanol or ethanol; the alkanol/diol mole ratio may then reach approximately 10.

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

The allyl alcohol concentration is not critical and can vary within wide limits.

30 At the end of the reaction or of the desired reaction time, the desired acid or diacid is recovered by any suitable means, for example by extraction.

The examples below illustrate the invention.

Examples 1 to 8; Control experiments (a) to (c)

35 A series of experiments is carried out according to the procedure described with reference to Example 1.

The following are introduced into a 125-cm³

Hastelloy B2 stainless steel autoclave purged beforehand with argon:

- 4.4 g (50 mmol) of 2-butene-1,4-diol
- 1 mg-at. of palladium in the form of PdCl_2
- 5 - 5 g of PBU_4Cl (17 mmol) and
- 25 cm^3 of acetonitrile

The autoclave is hermetically sealed, placed in an oven having an agitator and connected to a supply of gas under pressure. The reactor is purged in the cold
10 state with carbon monoxide and heated to 100°C ; the pressure is then adjusted to 125 bars. After 6 hours' reaction (except where otherwise stated), the autoclave is cooled and outgassed.

The reaction solution is diluted to 100 cm^3 by
15 adding solvent.

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

All the experiments correspond to a degree of conversion of 100 %, and formation of the various acids
20 which follow is observed:

- HD : mixture of 3-hexene- and 2-hexenedioic acids in which 3-hexenedioic acid is preponderant.
- $\text{C}_5\text{ac.}$: mixture of valeric, 2-methylbutyric, 3-pentenoic, 2-pentenoic and 4-pentenoic
25 acids in which 3-pentenoic acid is preponderant.
- Sat.C_6 : mixture of ethylsuccinic, methylglutaric and adipic acids in which methylglutaric
30 acid is preponderant.
- PDO : pentadienoic acid

of which the number of moles formed per 100 moles of butenediol introduced is shown for each group.

The particular conditions as well as the results
35 obtained appear in Table I below.

TABLE I

5	Ex. No.	Additive		Solvent	t(h)	Results (%)			
		Nature	mmol			HD	C ₅ ac.	Sat.C ₆	PDO
	a	-	0	CH ₃ CN		<2	60	16	1
10	b	PPh ₃	2	"		2	0	0	15
	1	PBu ₄ Cl	17	"	3	37	28	9	0.5
	2	PMe ₄ Cl	"	"		19	21	6	ND
	3	PPh ₄ Cl	"	"		39	30	12	"
	4	NBu ₄ Cl	"	"		30	30	14	"
15	c	PBu ₄ Br	"	"		4	48	15	"
	5*	PBu ₄ Cl	17	NMP	1	80	4	3	0
	6*	"	34	"	2	85	4	1	0.5
	7*	"	68	"	1.5	92	3	1	0
20	8	"	102	None	1.5	85	3	0.5	0

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

NMP : N-methylpyrrolidone

25 (*) : (PBu₄Cl + NMP) = 30 ml

ND : not determined

Examples 9 to 11:

In the autoclave and according to the procedure described above for Example 1, a second series of experiments is carried out, replacing a portion of the 2-butene-1,4-diol by an equivalent volume of solvent, keeping the total volume (solvent + butenediol)

constant and equal to 30 cm³. The particular conditions as well as the results obtained appear in Table II below.

TABLE II

Ex. No.	Butenediol mmol	Solvent	t(h)	Results (%)			
				HD	C ₅ ac.	Sat.C ₆	PDO
1	50	CH ₃ CN	3	37	28	9	0.5
9	25	"		53	18	13	0.5
5	50	NMP	1	80	4	3	0
10	25	"	1	85	4	2	0
11	100	"		75	2	1	2.5

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

NMP : N-methylpyrrolidone

Example 12:

Example 1 above is reproduced, replacing palladium chloride by an equivalent quantity of palladium in the form of Pd(OAc)₂.

In 6 hours' reaction, the following was obtained:

- HD: 24 %

Example 13:

Example 1 above is reproduced, replacing palladium chloride by an equivalent quantity of palladium in the

form of $\text{Pd}(\text{dba})_2$.

In 6 hours' reaction, the following was obtained:

- HD: 32 %

Example 14:

5 Example 1 above is reproduced, using an equivalent volume of dimethyl sulphoxide as a solvent.

In 6 hours' reaction, the following is obtained:

- HD: 70 %

Example 15:

10 Example 1 above is reproduced, using an equivalent volume of dimethylformamide as a solvent.

In 6 hours' reaction, the following is obtained:

- HD: 50 %

Example 16:

15 Example 5 above is reproduced, replacing palladium chloride by an equivalent quantity of palladium in the form of $\text{Pd}(\text{OAc})_2$.

In 6 hours' reaction, the following is obtained:

- HD: 45 %

20 Example 17:

Example 5 above is reproduced, replacing palladium chloride by an equivalent quantity of palladium in the form of $\text{Pd}(\text{dba})_2$.

In 21 hours' reaction, the following is obtained:

25 - HD: 85 %

Example 18:

Example 5 is reproduced, using 0.5 mg-at. of palladium (in the form of PdCl_2).

In 1 h 30 min, absorption has finished and substantially the same results are obtained:

- HD: 75%

Example 19:

5 Example 5 is reproduced, using 0.12 mg-at. of palladium (in the form of PdCl_2).

In 12 h, absorption has finished and substantially the same results are obtained:

- HD: 75 %

10 Example 20:

Example 5 above is reproduced, using an equivalent quantity of 1-butene-3,4-diol.

Substantially the same results are obtained:

- HD: 80 %

15 Example 21:

Example 5 above is reproduced, replacing palladium chloride by an equivalent quantity of palladium deposited on charcoal (3 % by weight of Pd on C).

20 In 1 hour, absorption has finished and the following is obtained:

- HD: 44 %

Example 22:

25 Example 5 above is reproduced, replacing palladium chloride by an equivalent quantity of PBu_4PdCl , and replacing PBu_4Cl by an equivalent volume of N-methylpyrrolidone.

In 15 min, absorption has finished and the following is obtained:

- HD: 45 %

Examples 23 to 27:

A series of experiments similar to Example 5 above is carried out, replacing N-methylpyrrolidone (NMP) by the same volume of an (NMP + water) or (NMP + methanol) mixture.

The particular conditions and the results obtained are collated in Table (III) below:

TABLE III

10

15

20

Ex. No.	Water (mmol)	Methanol (mmol)	t	HD %
23	50	-	40 min	74.5
24	100	-	6 h	85
25	200	-	1 h	78
26	-	100	1 h	78
27	-	200	50 min	70

t: absorption time.

Examples 28 to 38:

A series of experiments is carried out on a charge similar to that described in Example 1, using as a solvent either acetonitrile (Examples 28 to 32) or N-methylpyrrolidone (NMP) (Examples 33 to 38), modifying the reaction temperature ($T^{\circ}\text{C}$) or the carbon monoxide pressure measured at temperature $\{P(\text{CO})\}$.

30

The particular conditions and the results obtained appear in Table IV below.

TABLE IV

				Results (%)				
5	Ex. No.	P(CO) bars	T°C	t(h)	HD	C ₅ ac.	Sat.C ₆	PDO
10	28	60	100	4.5	20	28	12	0
	29	120	"	3	41	18	15	0
	30	180	"	3	44	13	2	0
	31	120	130	3	18	30	13	1
	32	"	70		43	5	2	2
15	33	15	100	(*)	15	46	2	2.5
	34	30	"		56	17	3	1.5
	35	60	"	2	80	6	1	2
	5	120	"	1	80	4	3	0
	36	180	"	2	82	2	0	3
20	37	120	130	0.66	55	14	2	2
	38	"	70		70	1	0	5

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

NMP : N-methylpyrrolidone

25 (*) : absorption time = 18 hours

Example 39:

In an apparatus and according to a procedure similar to that described above, an experiment is carried out on a charge consisting of:

30 - 50 mmol of allyl alcohol

- 37.5 cm³ of ethylbenzene
- 0.25 mg-at. of palladium introduced in the form of PdCl₂
- 2.5 mmol of PBu₄Cl

5 The temperature is 80°C and the pressure adjusted to 200 bars. After 6 hours' reaction, the autoclave is cooled and outgassed.

Analysis of the crude mixture by gas chromatography shows that the degree of conversion of allyl alcohol is 100 %, and that the mixture contains allyl vinylacetate (RY = 60 %; RY being defined by the ratio of twice the number of moles of vinylacetate detected to the number of moles of allyl alcohol introduced) and 3-butenic acid, the quantity of which, estimated as follows, is of the order of 30 % relative to the allyl alcohol introduced.

The estimation is carried out by difference between, on the one hand the total quantity of methyl ester assayed by gas chromatography after esterification, and on the other hand the quantity of methyl ester resulting from degradation of the allyl vinylacetate, analysis of the mixture, after esterification, by gas chromatography having led to the following results:

25	RY (allyl vinylacetate)	= 20 %
	RY (methyl 3-butenate)	= 50 %

(RY: molar yield relative to the substrate introduced)

Control experiment (d):

Example 39 above is reproduced, introducing an equivalent quantity of palladium in the form of the complex

5 $\text{PdCl}_2 (\text{PPh}_3)_2$

and replacing PBu_4Cl by an equivalent quantity of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

The results obtained, all conditions otherwise being equal, are as follows:

10 Analysis of the crude mixture:

Degree of conversion of allyl alcohol: 15 %

RY (allyl vinylacetate): 16 %

Analysis of the mixture after esterification:

RY (allyl vinylacetate): 8 %

15 RY (methyl 3-butenate): 6 %

Comparison of the results obtained in Example 39 (according to the invention) and in control experiment (d), respectively, demonstrates the fact that, with the process according to the invention, access is gained to

20 the β, γ -unsaturated acid, and with an improved efficiency of carbonylation.

Example 40:

In an apparatus and according to a procedure similar to that described above, an experiment is

25 carried out on a charge consisting of:

40 mmol of allyl alcohol

25 cm^3 of N-methylpyrrolidone

1 mmol of PdCl_2

17 mmol of PBu_4Cl

The temperature is 100°C and the pressure adjusted to 120 bars. After 30 min of reaction (absorption time), the results obtained are as follows:

5 Analysis of the crude mixture:

Degree of conversion of allyl alcohol: 100 %

RY (allyl vinylacetate): 0 %

Analysis of the mixture after esterification:

RY (allyl vinylacetate): 0 %

10 RY (methyl 3-butenate): 62 %

This example shows that the β,γ -unsaturated acid is formed selectively, and with an appreciable efficiency of carbonylation.

Example 41:

15 Example 40 above is reproduced, adding 100 mmol of water to the charge. After 10 minutes' reaction (absorption time), the results obtained are as follows:

Analysis of the crude mixture:

Degree of conversion of allyl alcohol: 100 %

20 RY (allyl vinylacetate): 2 %

Analysis of the mixture after esterification:

RY (allyl vinylacetate): 0 %

RY (methyl 3-butenate): 100 %

Control experiment (e):

25 Example 40 above is reproduced, replacing palladium chloride by an equivalent quantity of the complex $\text{PdCl}_2(\text{PPh}_3)_2$ and PBu_4Cl by 10 mmol of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$. After 4 hours' reaction (absorption time), the results

obtained are as follows:

Analysis of the crude mixture:

Degree of conversion of allyl alcohol: 10 %

RY (allyl vinylacetate): 2 %

5 Analysis of the mixture after esterification:

RY (allyl vinylacetate): 0 %

RY (methyl 3-butenate): 5 %

Examples 42 to 46:

In an autoclave and according to the procedure
10 described above, a series of experiments is carried out
starting with various allyl alcohols under the
following common condition:

The charge consists of:

- 50 mmol of alcohol whose nature is specified in
15 Table V below:

- 1 mg-at. of palladium in the form of PdCl_2 ,
- 17 mmol of PBU_4Cl
- 25 cm^3 of N-methylpyrrolidone

The reaction temperature is 100°C and the carbon
20 monoxide pressure measured at temperature is 120 bars.

At the end of the reaction, the crude reaction
mixture is analysed by gas chromatography and is then
esterified with methanol; the quantity of β,γ -
unsaturated acid is determined by gas chromatographic
25 assay of the corresponding methyl esters.

DC: represents the degree of conversion of the
alcohol in question.

RY: represents the number of moles of β,γ -

unsaturated acid formed per 100 moles of
alcohol introduced.

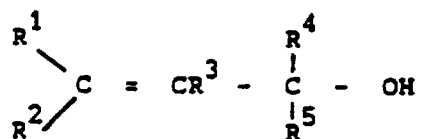
TABLE V

5					
	Ex. No.	Nature of the alcohol	t(h)	DC	RY
	42	2-Methyl-1-propen-3-ol	3.5	90	50
10	43	2-Buten-1-ol	3.5	100	92
	44	2-Cyclohexen-1-ol	3.5	100	82
	45	3-Phenyl-2-propen-1-ol	1	92	85
	46	3-Methyl-1-buten-3-ol	0.5	100	100

15

CLAIMS

1. Process for preparing β, γ -unsaturated acids by bringing an allyl alcohol, carbon monoxide and a palladium-based catalyst into contact at high temperature and under a pressure above atmospheric pressure, characterized in that the reaction is also performed in the presence of at least one quaternary onium chloride of a group VB element selected from nitrogen and phosphorus, the said element being four-coordinated to carbon atoms, it being possible for the nitrogen to be coordinated to two pentavalent phosphorus atoms.
2. Process according to claim 1, characterized in that the allyl alcohol corresponds to the formula (I):



in which:

. R^1 to R^5 , which may be identical or different, represent:

- a hydrogen atom,
- an alkyl, aryl or aralkyl radical containing at most 20 carbon atoms,
- an alkenyl radical free from terminal unsaturation and containing at most 15 carbon atoms,

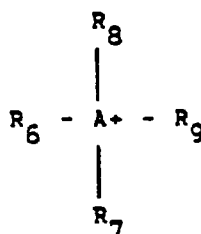


. any one of the radicals R^1 to R^5 can, in addition, represent a hydroxymethyl radical ($-\text{CH}_2\text{OH}$),

5 R^1 (or R^2) and R^4 (or R^5) together can, in addition, form a single divalent alkylene radical containing from 2 to 5 carbon atoms.

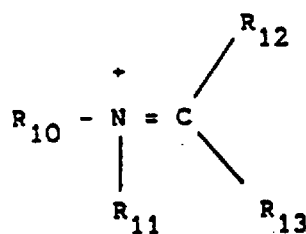
3. Process according to claim 1 or 2, characterized in that the quaternary onium chloride possesses a quaternary onium cation corresponding to one of the
10 formulae II to V below:

II)



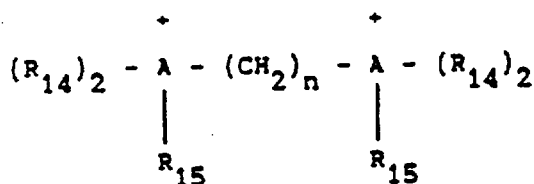
15

III)



20

IV)



25

V)





in which:

- A represents nitrogen or phosphorus;
- R_6 , R_7 , R_8 and R_9 are identical or different and represent:

5 . a linear or branched alkyl radical containing from 1 to 16 carbon atoms, optionally substituted with a phenyl, hydroxy, halo, nitro, alkoxy or alkoxy-carbonyl group;

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

 . an aryl radical containing from 6 to 10 carbon atoms, optionally substituted with one or more alkyl radicals containing from 1 to 4 carbon atoms, or
15 alkoxy, alkoxycarbonyl or halo radicals;

 . it being possible for two of the said radicals R_6 to R_9 together to form a linear or branched alkylene, alkenylene or alkadienylene radical containing from 3 to 6 carbon atoms;

20 - R_{10} , R_{11} , R_{12} and R_{13} are identical or different and represent:

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

 . it being possible for the radicals R_{12} and R_{13}
25 together to form an alkylene radical containing from 3 to 6 carbon atoms;

 . it being possible for the radicals R_{11} and R_{12} or R_{11} and R_{13} together to form an alkylene, alkenylene or



alkadienylene radical containing 4 carbon atoms and constituting with N a nitrogenous heterocycle;

- R_{14} represents a linear or branched alkyl radical containing from 1 to 4 carbon atoms or a phenyl

5 radical;

- R_{15} represents:

. a linear or branched alkyl radical containing from 1 to 4 carbon atoms, similar to or different from R_{14} ;

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

- n represents an integer not less than 1 and not more than 10, and preferably not more than 6;

15 - R_{16} represents an aryl radical containing from 6 to 10 carbon atoms, optionally substituted with one or more alkyl groups containing from 1 to 4 carbon atoms, or alkoxy, alkoxycarbonyl or halo groups.

4. Process according to any one of the preceding
20 claims, characterized in that the quaternary onium cation corresponds to the formula II given in claim 3, in which:

- A represents phosphorus, and

- R_6 , R_7 , R_8 and R_9 are identical or different

25 and represent a linear or branched alkyl radical containing from 1 to 8 carbon atoms, or a phenyl or 4-methylphenyl radical.

5. Process according to any one of the preceding



claims, characterized in that the quaternary onium chloride is tetrabutylphosphonium chloride.

6. Process according to any one of the preceding claims, characterized in that the mole ratio of the
5 onium cation to palladium is not less than 1.

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

10 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
15 claims, characterized in that the pressure is between 10 and 250 bars (1,000 and 25,000 kPa), and preferably between 15 and 180 bars (1,500 and 18,000 kPa).

10. Process according to any one of the preceding claims, characterized in that the reaction is performed
20 in the presence of an organic diluent or solvent.

11. Process according to claim 10, characterized in that the solvent is N-methylpyrrolidone.

12. Process according to claim 10, characterized in that the solvent is the quaternary onium chloride.

25 13. Process according to any one of the preceding claims, characterized in that the allyl alcohol is selected from 2-butene-1,4-diol, 1-butene-3,4-diol and mixtures thereof.



14. Process according to claim 13, characterized in that the reaction is performed in the presence of a lower alkanol.

15. Process according to claim 13, characterized in
5 that the reaction is performed in the presence of water.