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PROCESS FOR THE CARBONYLATION OF ALLYLIC BUTENOLS

AND OF THEIR ESTERS

The present invention relates to the carbonylation, with the aid of carbon monoxide, of allylic butenols and/or of their carboxylic esters.

Patent US-A-4,801,743 describes the carbonylation of allyl alcohol by carbon monoxide, in the presence of a palladium catalyst and of a promoter chosen from hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide.

Patent EP-A-0,428,979 describes the carbonylation of allylic butenols and of their esters, in the presence of a rhodium catalyst and of a promoter chosen from hydrogen bromide and hydrogen iodide, the promoter/rhodium molar ratio being between 1:1 and 10:1.

A new process for the carbonylation of allylic butenols and/or of their carboxylic esters has now been found, which consists in reacting carbon monoxide with at least one of the said allylic butenols and carboxylic esters, at elevated temperature, under a pressure greater than atmospheric pressure and in the presence of an iridium catalyst and of an iodinated or brominated promoter, the promoter/iridium molar ratio being between 0.1:1 and 20:1.

The activity of iridium catalysts in this reaction is surprising, because iridium is not known to catalyse the hydroxycarbonylation of butadiene,

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palladium or rhodium catalysts being generally used for this reaction.

The allylic butenols are 3-buten-2-ol, 2-buten-1-ol and their mixtures; the butenol esters which
5 are used in the process of the invention are essentially the carboxylates of these butenols and more particularly those which are derived from saturated or unsaturated aliphatic carboxylic acids having 1 to 12 carbon atoms. By way of nonlimiting examples, there may
10 be mentioned the allylic butenol esters of acetic acid, of propionic acid, of valeric acid, of adipic acid and of pentenoic acids (2-pentenoic, 3-pentenoic and 4-pentenoic acids).

Preferentially, the allylic butenols and/or
15 their acetates, their valerates or their pentenoates will be used as a substrate. In practice it is preferable, when a butenol ester is used, to choose esters of carboxylic acids which are capable of being formed in the course of the carbonylation reaction,
20 such as valeric acid or 3-pentenoic acid.

The allylic butenols are compounds which are commercially available; they may also be easily prepared by hydration of butadiene. Their esters may be obtained by reaction of the said butenols or of
25 butadiene with the chosen carboxylic acid. These preparations of the substrates may be performed extemporaneously or in the carbonylation reactor itself.

Various sources of iridium are capable of being used for the iridium catalyst necessary in the present process.

As examples of such sources of iridium, there may be mentioned:

- metallic Ir; IrO_2 ; Ir_2O_3 ;
- IrCl_3 ; $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$;
- IrBr_3 ; $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$;
- IrI_3 ;
- 10 - $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
- $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
- $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
- 15 - $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
- $\text{Ir}(\text{acac})(\text{CO})_2$;
- $[\text{IrCl}(\text{cod})]_2$;

(acac = acetylacetonate; cod = 5-cyclooctadiene).

The iridium catalysts which are more particularly suitable are:

$[\text{IrCl}(\text{cod})]_2$, $\text{Ir}_4(\text{CO})_{12}$ and $\text{Ir}(\text{acac})(\text{CO})_2$.

The quantity of catalyst to be used may vary within wide limits.

In general a quantity, expressed in moles of iridium metal per litre of reaction mixture, of between 25 10^{-4} and 10^{-1} leads to satisfactory results. Smaller quantities may be used, although it is observed, however, that the reaction rate is low. Larger

quantities have no disadvantages other than from the economic viewpoint.

The iridium concentration in the reaction mixture is preferably between 5×10^{-4} and 5×10^{-2} mol/litre.

Iodinated or brominated promoter is understood to mean, within the context of the process, hydrogen iodide, hydrogen bromide and the organoiodine and organobromine compounds which are capable of generating respectively hydrogen iodide and hydrogen bromide under the reaction conditions; these organoiodine and organobromine compounds are more particularly alkyl iodides and bromides having from 1 to 10 carbon atoms, among which methyl iodide and methyl bromide are preferred.

The promoter/Ir molar ratio is preferably between 1:1 and 10:1.

It is also possible to complement the catalyst system consisting of the actual iridium catalyst and the promoter with an effective quantity of a copromoter such as a metal iodide or a metal bromide, or else a metal carboxylate which is capable of being converted, at least partially, into the corresponding iodide or bromide in the reaction mixture. This copromoter can especially be an alkali metal iodide or bromide, or an alkali metal acetate. Thus it is favourable, in particular with regard to the activity of the catalyst, to use lithium iodide, sodium iodide,

lithium bromide, sodium bromide, lithium acetate or sodium acetate. The copromoter/promoter molar ratio may vary very greatly, for example from 0.01:1 to 100:1 and preferably from 0.1:1 to 50:1.

5 The reaction is carried out in liquid phase. The temperature at which the reaction is carried out is generally from 50°C to 250°C, and preferably from 80°C to 200°C.

 The total pressure at the reaction
10 temperature may vary within wide limits. The partial pressure of the carbon monoxide, measured at 25°C, is generally from 0.5 bar to 100 bar, and preferably from 1 bar to 50 bar. The carbon monoxide used may be substantially pure carbon monoxide or technical-grade
15 carbon monoxide, such as are found commercially.

 The reaction for the carbonylation of allylic butenols and/or of their esters is generally carried out in a solvent.

 As solvent, there may especially be used the
20 saturated or unsaturated aliphatic or aromatic carboxylic acids containing not more than 20 carbon atoms, insofar as they are liquid under the reaction conditions. As examples of such carboxylic acids, there may be mentioned acetic acid, propionic acid, butanoic
25 acid, valeric acid, adipic acid, pentenoic acids, benzoic acid and phenylacetic acid. When an allylic butenol ester is carbonylated, it is wise to use as solvent the carboxylic acid corresponding to the ester.

Other classes of solvents may also be used, especially saturated aliphatic or cycloaliphatic hydrocarbons and their chlorinated derivatives, insofar as they are liquid under the reaction conditions. As
5 examples of such solvents, there may be mentioned benzene, toluene, chlorobenzene, dichloromethane, hexane and cyclohexane.

When it is present in the reaction mixture, the solvent represents for example from 10 % to 99 % by
10 volume relative to the total volume of the said reaction mixture, and preferably from 30 % to 90 % by volume.

The process of carbonylation according to the invention allows pentenoic acids, in particular
15 3-pentenoic acid in the form of its cis and trans isomers, and to a lesser extent 2-pentenoic acid, to be prepared. These pentenoic acids may themselves be hydroxycarbonylated by carbon monoxide and water to give adipic acid, one of the starting materials in the
20 preparation of polyamides 6,6.

As the hydroxycarbonylation of pentenoic acids may advantageously be carried out in the presence of an iridium catalyst and of an iodinated or brominated promoter, it is possible, where appropriate,
25 to proceed to this second reaction directly using the reaction mixture resulting from the carbonylation of the allylic butenols and/or of their esters, or after a brief separation of the reaction by-products, using the

same apparatus. It is also possible to treat the reaction mixture according to any appropriate technique to separate the pentenoic acids obtained, the catalyst system, the solvent where present and the various by-products formed.

The process of the invention may be carried out continuously or noncontinuously.

The examples which follow illustrate the invention.

10 EXAMPLE 1

Into a 125 cm³ autoclave purged beforehand with argon, there are successively introduced:

- crotyl valerate (2-butenyl pentanoate): 50 mmol
- valeric acid (PA): 46
- 15 cm³
- hydrogen iodide (in aqueous solution at a concentration of 57 % by weight): 1.5 mmol
- [IrCl(cod)]₂: 0.5 mmol
- 20 - LiI: 15 mmol

The autoclave is closed, placed in an oven incorporating agitation and connected to the supply of CO under pressure. 5 bar of CO are applied at 25°C, then the system is heated to 140°C. The pressure is adjusted at this temperature to 50 bar with the aid of CO (which corresponds to 36 bar of partial pressure of CO measured at 25°C) and this pressure is maintained

for 2 hours at 140°C.

The autoclave is then cooled and degassed, and the reaction mixture is analysed by gas chromatography (GC).

5 The following results are obtained:

- extent of conversion (EC) of crotyl valerate: 35 %
- yield of 3-pentenoic acid (P3) relative to the crotyl valerate charged (RY): 24 %

10 Other compounds were identified by GC:

- 2-methyl-3-butenic acid (MBE)
- 2-methylbutanoic acid (MBA)
- butenes (C4)
- valeric acid.

15 EXAMPLE 2

Example 1 is reproduced with replacement of the hydrogen iodide and lithium iodide by 1.5 mmol of hydrogen bromide.

The following results are obtained:

- 20 - EC of crotyl valerate: 80 %
- RY of P3: 40 %

EXAMPLES 3 to 7

Example 1 is reproduced using variable amounts of hydrogen iodide and lithium iodide (shown in 25 the table below). In addition, Example 7 was carried out at 185°C instead of 140°C. The results obtained are collated in the table below.

Examples	HI (mmol)	LiH (mmol)	% EC of crotyl valerate	% RY P3	% RY MBE + MBA	% RY C4
Example 3	1.5	0	48	16	20	15
Example 4	4.0	15	63	29	5	7
Example 5	0.5	15	48	10	4	6
Example 6	1.5	30	70	24	4	12
Example 7	1.5	0	80	17	13	18

EXAMPLE 8

Example 1 is reproduced with replacement of crotyl valerate by 2-buten-1-ol (or crotyl alcohol) and with omission of lithium iodide.

The following results are obtained:

- EC of 2-buten-1-ol: 100 %
- RY of P3: 24 %

EXAMPLE 9

Into a 125 cm³ autoclave purged beforehand with argon, there are successively introduced:

- 2-butenyl 3-pentenoate: 50 mmol
- acetic acid: 46 cm³
- hydrogen bromide: 1.5 mmol
- [IrCl(cod)]₂: 0.5 mmol
- NaCH₃COO: 3 mmol

The autoclave is closed, placed in an oven

incorporating agitation and connected to the supply of CO under pressure. 5 bar of CO are applied at 25°C, then the system is heated to 140°C. The pressure is adjusted at this temperature to 50 bar with the aid of CO (which corresponds to 36 bar of partial pressure of CO measured at 25°C), and this pressure is maintained for 1 hour 30 min at 140°C.

The autoclave is then cooled and degassed, and the reaction mixture is analysed by gas chromatography (GC).

The following results are obtained:

	- EC of 2-butenyl 3-pentenoate:	31 %
	- RY of P3:	15 %
	- RY of C4:	4 %
15	- RY of butadiene:	1 %
	- RY of C6 diacids:	1 %

COMPARATIVE TEST 1

Into a 125 cm³ autoclave purged beforehand with argon, there are successively introduced:

20	- butadiene:	80 mmol
	- water:	90 mmol
	- valeric acid:	46 cm ³
	- hydrogen iodide:	1.5 mmol
	- [IrCl(cod)] ₂ :	0.5 mmol

The autoclave is closed, placed in an oven incorporating agitation, and connected to the supply of CO under pressure. 5 bar of CO are applied at 25°C, then the system is heated to 140°C. The pressure is

adjusted at this temperature to 50 bar with the aid of CO (which corresponds to 36 bar of partial pressure of CO measured at 25°C), and this pressure is maintained for 2 hours at 140°C.

- 5 The autoclave is then cooled and degassed, and the reaction mixture is analysed by gas chromatography (GC).

The following results are obtained:

	- EC of butadiene:	100 %
10	- RY of P3:	6 %
	- RY of C4:	32 %
	- RY of valeric acid:	6 %
	- RY of MBA + MBE:	9 %

CLAIMS

1) Process for the carbonylation of allylic butenols and/or their carboxylic esters, characterized in that carbon monoxide is reacted with at least one of the said allylic butenols and carboxylic esters, at elevated temperature, under a pressure greater than atmospheric pressure, and in the presence of an iridium catalyst and of an iodinated or brominated promoter, the promoter/iridium molar ratio being between 0.1:1 and 20:1.

2) Process according to Claim 1, characterized in that the allylic butenols are 3-buten-2-ol, 2-buten-1-ol and their mixtures, and the butenol esters are the carboxylates of these butenols which are derived from saturated or unsaturated aliphatic carboxylic acids having 1 to 12 carbon atoms.

3) Process according to one of Claims 1 and 2, characterized in that the allylic butenol esters used are the allylic butenol esters of acetic acid, of propionic acid, of valeric acid, of adipic acid or of pentenoic acids.

4) Process according to one of Claims 1 to 3, characterized in that the iridium catalyst is chosen from the following various sources of iridium:

- metallic Ir; IrO_2 ; Ir_2O_3 ;
- IrCl_3 ; $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$;
- IrBr_3 ; $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$;
- IrI_3 ;



- $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
- $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
- 5 - $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
- $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
- $\text{Ir}(\text{acac})(\text{CO})_2$;
- $[\text{IrCl}(\text{cod})]_2$.

5) Process according to one of Claims 1 to
 10 4, characterized in that the quantity of iridium catalyst used, expressed in moles of iridium metal per litre of reaction mixture, is between 10^{-4} and 10^{-1} , and is preferably between 5×10^{-4} and 5×10^{-2} mol/litre.

6) Process according to one of Claims 1 to
 15 5, characterized in that the iodinated or brominated promoter is chosen from hydrogen iodide, hydrogen bromide and the organoiodine and organobromine compounds which are capable of generating respectively hydrogen iodide and hydrogen bromide under the reaction
 20 conditions.

7) Process according to one of Claims 1 to 6, characterized in that the promoter/Ir molar ratio is preferably between 1:1 and 10:1.

8) Process according to one of Claims 1 to
 25 7, characterized in that the catalyst system consisting of the actual iridium catalyst and the promoter is complemented with an effective quantity of a copromoter such as a metal iodide or a metal bromide, or a metal



carboxylate which is capable of being converted, at least partially, into the corresponding iodide or bromide in the reaction mixture, preferably an alkali metal iodide or bromide or an alkali metal acetate.

5 9) Process according to Claim 8, characterized in that the copromoter/promoter molar ratio is from 0.01:1 to 100:1 and preferably from 0.1:1 to 50:1.

10 10) Process according to one of Claims 1 to 9, characterized in that the reaction is carried out in liquid phase, at a temperature of from 50°C to 250°C and preferably from 80°C to 200°C and at a partial pressure of carbon monoxide, measured at 25°C, of from 0.5 bar to 100 bar, and preferably from 1 bar to 15 50 bar.

 11) Process according to one of Claims 1 to 10, characterized in that the carbonylation reaction is carried out in a solvent chosen from saturated or unsaturated aliphatic or aromatic carboxylic acids 20 containing not more than 20 carbon atoms, saturated aliphatic or cycloaliphatic hydrocarbons and their chlorinated derivatives which are liquid under the reaction conditions.

 12) Process according to Claim 11, 25 characterized in that the solvent is chosen from acetic acid, propionic acid, butanoic acid, valeric acid, adipic acid, pentenoic acids, benzoic acid, phenylacetic acid, benzene, toluene, chlorobenzene,



dichloromethane, hexane and cyclohexane.

13) Process according to one of Claims 11
and 12, characterized in that the solvent represents
from 10 % to 99 % by volume relative to the total
5 volume of the reaction mixture, and preferably from 30
% to 90 % by volume.

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PROCESS FOR THE CARBONYLATION OF ALLYLIC BUTENOLS
AND OF THEIR ESTERS

COMPANY KNOWN AS RHONE-POULENC CHIMIE

ABSTRACT

The present invention relates to the carbonylation with the aid of carbon monoxide of allylic butenols and/or of their carboxylic esters.

It consists more precisely in reacting carbon monoxide with at least one of the said allylic butenols and carboxylic esters, at elevated temperature, at a pressure greater than atmospheric pressure and in the presence of an iridium catalyst and of an iodinated or brominated promoter, the promoter/iridium molar ratio being between 0.1:1 and 20:1.

This process makes possible the preparation of pentenoic acids, in particular 3-pentenoic acid, which may itself be hydroxycarbonylated by the carbon monoxide and the water to adipic acid.

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PROCESS FOR THE CARBONYLATION OF ALLYLIC BUTENOLS

AND OF THEIR ESTERS

The present invention relates to the carbonylation, with the aid of carbon monoxide, of allylic butenols and/or of their carboxylic esters.

Patent US-A-4,801,743 describes the carbonylation of allyl alcohol by carbon monoxide, in the presence of a palladium catalyst and of a promoter chosen from hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide.

Patent EP-A-0,428,979 describes the carbonylation of allylic butenols and of their esters, in the presence of a rhodium catalyst and of a promoter chosen from hydrogen bromide and hydrogen iodide, the promoter/rhodium molar ratio being between 1:1 and 10:1.

A new process for the preparation of pentenoic acids by the carbonylation of allylic butenols and/or of their carboxylic esters has now been found, which consists in reacting carbon monoxide with at least one of the said allylic butenols and carboxylic esters, at elevated temperature, under a pressure greater than atmospheric pressure and in the presence of an iridium catalyst and of an iodinated or brominated promoter, the promoter/iridium molar ratio being between 0.1:1 and 20:1.

The activity of iridium catalysts in this reaction is surprising, because iridium is not known to catalyse the hydroxycarbonylation of butadiene,

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CLAIMS

1) Process for the preparation of pentenoic acids by the carbonylation of allylic butenols and/or their carboxylic esters, characterized in that carbon monoxide is reacted with at least one of the said allylic butenols and carboxylic esters, at elevated temperature, under a pressure greater than atmospheric pressure, and in the presence of an iridium catalyst and of an iodinated or brominated promoter, the promoter/iridium molar ratio being between 0.1:1 and 20:1.

2) Process according to Claim 1, characterized in that the allylic butenols are 3-buten-2-ol, 2-buten-1-ol and their mixtures, and the butenol esters are the carboxylates of these butenols which are derived from saturated or unsaturated aliphatic carboxylic acids having 1 to 12 carbon atoms.

3) Process according to one of Claims 1 and 2, characterized in that the allylic butenol esters used are the allylic butenol esters of acetic acid, of propionic acid, of valeric acid, of adipic acid or of pentenoic acids.

4) Process according to one of Claims 1 to 3, characterized in that the iridium catalyst is chosen from the following various sources of iridium:

- metallic Ir; IrO_2 ; Ir_2O_3 ;
- IrCl_3 ; $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$;
- IrBr_3 ; $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$;
- IrI_3 ;



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dichloromethane, hexane and cyclohexane.

13) Process according to one of Claims 11 and 12, characterized in that the solvent represents from 10 % to 99 % by volume relative to the total volume of the reaction mixture, and preferably from 30 % to 90 % by volume.

14) Process for the preparation of adipic acid, characterized in that a pentenoic acid prepared by a process according to any one of the preceding claims is hydroxycarbonylated by carbon monoxide and water.



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