

PROCESS FOR THE HYDROXYCARBONYLATION OF LACTONES

The present invention relates to a process for the hydroxycarbonylation of lactones, more precisely of various valerolactones and of their
5 isomers, by reaction with carbon monoxide and water, to form the corresponding diacid.

The hydroxycarbonylation of pentenoic acids to prepare adipic acid always leads to the formation of greater or lesser amounts of gamma-valerolactone, as a
10 by-product of the reaction.

The commercial development of gamma-valerolactone (or 4-methylbutyrolactone) thus represents an important problem to be solved, within the framework of an industrial process for the
15 preparation of adipic acid by hydroxycarbonylation of pentenoic acids.

In Patent JP-A-54/092913 a process is described for the preparation of dicarboxylic acids by hydroxycarbonylation of lactones, in the presence of a
20 rhodium catalyst and of an iodinated promoter.

Patent EP-A-0,395,038, published a few years after the preceding patent, describes a similar process characterized by the choice of a region of temperature and of carbon monoxide pressure, as well as by a rapid
25 termination of the reaction as soon as the absorption of carbon monoxide rapidly diminishes, which allows, according to the patent in question, better yields of linear dicarboxylic acid to be obtained.

The present invention is characterized by the use of iridium, a different catalyst to that which was described previously for this reaction.

More specifically, it consists in a process
5 for the hydroxycarbonylation of at least one lactone having 5 carbon atoms by carbon monoxide and water, characterized in that the procedure is carried out in the presence of an effective quantity of an iridium catalyst and of an iodinated or brominated promoter,
10 the promoter/Ir molar ratio being between 0.1:1 and 20:1.

The lactones which may be used in the process of the invention are more particularly gamma-valerolactone (or 4-methylbutyrolactone), delta-
15 valerolactone, 2-methylbutyrolactone, 3-ethylpropiolactone, 2-ethylpropiolactone and 2,3-dimethylpropiolactone.

Among these lactones, gamma-valerolactone is the most interesting on account of its formation in the
20 processes for the hydroxycarbonylation of 3-pentenoic acid to give adipic acid.

It is possible, where appropriate, to use mixtures of the lactones indicated earlier; the lactones used may contain a quantity, which is not
25 critical, of other compounds such as pentenoic acids, valeric acid, adipic acid, 2-methylglutaric acid or 2-ethylsuccinic acid.

Various sources of iridium are capable of

being used for the iridium catalyst necessary in the present process.

By way of examples of such sources of iridium, there may be mentioned:

- 5 - 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 ;
 - $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
 - 10 - $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
 - $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
 - $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
 - 15 - $\text{Ir}(\text{acac})(\text{CO})_2$;
 - $[\text{IrCl}(\text{cod})]_2$;
- (acac = acetylacetonate; cod = 1,5-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 10^{-4} and 1 leads to satisfactory results. Smaller quantities may be used but a slow reaction rate is, however, observed. Larger quantities are only

inconvenient from the economic viewpoint.

Preferably, the iridium concentration in the reaction mixture is between 5×10^{-4} and 10^{-1} mol/litre.

Iodinated or brominated promoter is understood to mean, within the context of the process, hydrogen iodide, hydrogen bromide and organoiodine and organobromine compounds which are capable of generating respectively hydrogen iodide and hydrogen bromide under the reaction conditions; these organo-iodine and organobromine compounds are more particularly alkyl iodides and bromides having 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.

The reaction is carried out in the liquid phase. The temperature at which the procedure is carried out is generally from 100°C to 300°C and preferably from 150°C to 250°C .

The total pressure at the reaction temperature may vary within wide limits. The partial pressure of carbon monoxide, measured at 25°C , is generally from 0.5 bar to 100 bar and preferably from 1 bar to 80 bar.

The carbon monoxide used can be substantially pure carbon monoxide or technical-grade carbon monoxide, such as are found commercially.

Water is necessary for the hydroxycarbonylation of the lactones. Generally the

water/lactone molar ratio lies between 0.01 and 10.

A larger quantity is not desirable on account of the observed loss of catalytic activity. The water/lactone molar ratio can be momentarily lower than the minimum
5 value indicated earlier, for example if a continuous injection of water is performed, rather than its complete introduction with the other charges before the hydroxycarbonylation reaction.

Preferably, the water/lactone molar ratio is
10 between 0.05 and 2, the above comment relating to the minimum value being equally valid.

Another parameter is also of importance: this is the water concentration in the reaction mixture. This concentration is preferably maintained at a value
15 of 0.01 mol/litre to 3 mol/litre and for better efficiency of the reaction at a value of 0.01 mol/litre to 2 mol/litre.

As indicated earlier, this concentration can at a given moment be less than the lower limits
20 indicated, if a continuous injection of water is performed.

The hydroxycarbonylation reaction of the lactones is carried out either in the lactone itself as the liquid reaction medium, or in an independent
25 solvent.

As independent solvent, it is possible in particular to use 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 acid, valeric acid, adipic acid, pentenoic acids, benzoic acid and phenylacetic acid.

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

Mixtures of solvents may be used.

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

The hydroxycarbonylation process according to the reaction enables the commercial development of lactones bearing 5 carbon atoms, especially gamma-valerolactone which is formed in greater or lesser amounts during the hydroxycarbonylation of pentenoic acids. This allows an increase in the overall yield of a process for the preparation of adipic acid starting from butadiene via pentenoic acids, adipic acid being one of the starting materials in the preparation of polyamides 6-6.

The final reaction mixture is treated according to conventional methods used in chemistry, in order to separate the various compounds formed and the lactone which has not reacted, the latter being able to be subjected to a further hydroxycarbonylation.

The process according to the reaction may be implemented continuously or non continuously. When the process is performed continuously, the relative ratios of the reagents, catalyst, promoter and solvent can be fixed at an optimal value by those skilled in the art, whereas generally, in a process implemented non-continuously, these various ratios change as a function of the gradual conversion of the reactants.

The following examples illustrate the invention.

EXAMPLE 1

Into a 50 cm³ glass bulb, purged beforehand with argon, there are introduced successively:

	- gamma-valerolactone (VAL):	20 mmol
20	- water	20 mmol
	- acetic acid (AcOH):	10 cm ³
	- hydrogen bromide (in aqueous solution at 47% concentration by weight)	2.1 mmol
25	- IrCl ₃ :	0.23 mmol

The glass bulb is placed in a 125 cm³ autoclave, purged beforehand with argon. The autoclave is closed, placed in an oven incorporating agitation

and connected to the supply of CO under pressure. The system is placed under 5 bar of CO at 25°C, and is then heated to 220°C. The pressure is adjusted, at this temperature, to 100 bar with the aid of CO (which
 5 corresponds to 54 bar of partial pressure of CO measured at 25°C) and this pressure is maintained for 11 hours at 220°C.

The autoclave is then cooled and degassed and the reaction mixture is analysed by gas chromatography
 10 (GC) and by high performance liquid chromatography (HPLC).

The following results are obtained:

- degree of conversion (DC) of VAL: 97 %
- yield of adipic acid (A1) relative
 15 to VAL charged (RY): 43 %
- RY of 2-methylglutaric acid (A2): 15 %
- RY of 2-ethylsuccinic acid (A3): 3 %
- RY of valeric acid (PA): 19 %

EXAMPLE 2

20 Example 1 is repeated with the following changes:

- total pressure at 220°C of 28 bar (which corresponds to partial pressure of CO at 25°C of 11 bar) instead of 100 bar;
- 25 - holding period at 220°C of 2 hours instead of 11 hours.

The following results are obtained:

- degree of conversion (DC) of VAL: 68 %

- RY of adipic acid (A1): 40 %
- RY of 2-methylglutaric acid (A2): 9 %
- RY of 2-ethylsuccinic acid (A3): 3 %
- RY of valeric acid (PA): 14 %
- 5 - degree of linearity (ratio of
adipic acid formed/total of diacids
formed): 77 %
- space time yield of adipic acid
formed: 58 g l⁻¹h⁻¹

10 EXAMPLE 3

Example 2 is repeated with replacement of acetic acid by gamma-valerolactone itself: 11.8 g in total. The partial pressure of CO at 25°C (PCO25°) is 16 bar.

15 The following results are obtained:

- degree of conversion (DC) of VAL: 11 %
- yield of adipic acid (A1) relative
to VAL converted (CY): 26 %
- CY of 2-methylglutaric acid (A2): 10 %
- 20 - CY of 2-ethylsuccinic acid (A3): 14 %
- CY of valeric acid (PA): 15 %

EXAMPLES 4 TO 9

Example 1 is repeated, with the changes shown in the table below.

25 The results obtained are collated in the table below.

The abbreviations used in the table are those which have been shown previously in the examples.

Examples	VAL (in mmol)	Catalyst (in mmol)	Water (in mmol)	Promoter (in mmol)	Solvent (cm ³)	Temperature (°C)	Time at temperature	Total pressure P CO 25°	Results obtained				
									DC % VAL	RY % A ₁	RY % A ₂	RY % A ₃	RY % PA
Example 4	20	Ir ₄ CO ₁₂	32	HI	AcOH	180	17 h	45 bar	34	12	3	0	18
		0.53		2.5	10			26 bar					
Example 5	20	[IrCl(cod)] ₂	32	HI	AcOH	180	17 h	45 bar	55	23	7	1	14
		0.53		1.4	10			26 bar					
Example 6	118	IrCl ₃	20	HI	-	220	2 h	28 bar	9	7°	14°	13°	19°
		0.23		2.6	-			16 bar					
Example 7	118	[IrCl(cod)] ₂	32	HI	-	230	20 min	45 bar	49	30°	14°	3°	20°
		0.53		1.4	-			26 bar					
Example 8	118	[IrCl(cod)] ₂	32	HI	-	185	5 h	100 bar	36	43°	9°	2°	23°
		0.53		1.4	-			64 bar					
Example 9	118	[IrCl(cod)] ₂	32	HI	-	185	2 h	45 bar	28	54°	10°	0°	12°
		0.53		1.4	-			29 bar					

* CY % instead of RY %

EXAMPLE 10

Example 1 is repeated, with the following charges and operating conditions:

- gamma-valerolactone (VAL): 110 mmol
- 5 - total water 12 mmol
- hydrogen iodide (in aqueous solution at 57% concentration by weight) 0.384 mmol
- $\text{IrCl}(\text{cod})_2$: 0.156 mmol

10 The initial water concentration is 1 mol/litre.

The temperature is 200°C; the total pressure at this temperature is 50 bar (equivalent to a partial pressure of CO at 25°C of 30 bar); the duration of the reaction at this temperature is 1 hour.

The following results are obtained:

- degree of conversion 16 % (equivalent to (DC) of VAL: 100% conversion of the water)
- 20 - yield of adipic acid (A1) relative to VAL converted (CY): 52 %
- CY of 2-methylglutaric acid (A2): 10 %
- CY of 2-ethylsuccinic acid (A3): 3 %
- CY of valeric acid (PA): 8 %
- 25 - CY of pentenoic acids: 15 %
- CY of 2-methylbutyric acid: 1 %
- space time yield of A1: 118 $\text{gl}^{-1}\text{h}^{-1}$
- degree of linearity of A1: 83 %

EXAMPLE 11

Example 10 is repeated, with 24 mmol of water instead of 12 mmol.

The initial water concentration is
5 2 mol/litre.

The reaction time is 3 hours.

The following results are obtained:

- degree of conversion (DC) of VAL: 17 %
- CY of A1: 48 %
- 10 - space time yield of A1: 40 g l⁻¹h⁻¹
- degree of linearity: 74 %

COMPARATIVE TEST 1

Example 2 is repeated with replacement of IrCl₃ by the same molar quantity of RhCl₃; the test is
15 maintained for 11 h at 220°C in order to obtain an
degree of conversion comparable to that of Example 2.

The following results are obtained

- degree of conversion (DC) of VAL: 79 %
- RY of adipic acid (A1): 51 %
- 20 - RY of 2-methylglutaric acid (A2): 21 %
- RY of 2-ethylsuccinic acid (A3): 3 %
- RY of valeric acid (PA): 2 %
- space time yield of A1: 14 g h⁻¹l⁻¹
- degree of linearity: 68 %

25 It is noted that the degree of linearity is
greater with iridium (Example 2) than with rhodium
(77 % as opposed to 68 %).

In addition, the test with rhodium, despite a

much longer reaction time (11 h as opposed to 2 h),
leads to a space time yield of adipic acid which is
quite clearly smaller than in Example 2 with iridium.

CLAIMS

1. Process for the hydroxycarbonylation of at least one lactone having 5 carbon atoms by carbon monoxide and water, characterized in that the procedure is carried out in the presence of an effective quantity of an iridium catalyst and of an iodinated or brominated promoter, the promoter/Ir molar ratio being between 0.1:1 and 20:1.
2. Process according to Claim 1, characterized in that the lactone used is chosen from gamma-valerolactone, delta-valerolactone, 2-methylbutyrolactone, 3-ethylpropiolactone, 2-ethylpropiolactone and 2,3-dimethylpropiolactone and is preferably gamma-valerolactone.
3. Process according to one of Claims 1 and 2, characterized in that the iridium catalyst used is chosen from:
- 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 ;
 - $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
 - $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
 - $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
 - $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
 - $\text{Ir}(\text{acac})(\text{CO})_2$;



- $[\text{IrCl}(\text{cod})]_2$.

4. Process according to one of Claims 1 to 3, characterized in that the quantity of catalyst, expressed in moles of iridium metal per litre of
5 reaction mixture, is between 10^{-4} and 1 and preferably between 5×10^{-4} and 10^{-1} mol/litre.
5. Process according to one of Claims 1 to 4, characterized in that the iodinated or brominated promoter is chosen from hydrogen iodide, hydrogen
10 bromide and the organoiodine and organobromine compounds capable of generating respectively hydrogen iodide and hydrogen bromide under the reaction conditions.
6. Process according to one of Claims 1 to 5,
15 characterized in that the promoter/Ir molar ratio is between 1:1 and 10:1.
7. Process according to one of Claims 1 to 6, characterized in that the reaction is carried out in the liquid phase at a temperature of 100°C to 300°C and
20 preferably from 150°C to 250°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 80 bar.
8. Process according to one of Claims 1 to 7, characterized in that the water/lactone molar ratio
25 lies between 0.01 and 10 and is preferably between 0.05 and 2.
9. Process according to one of Claims 1 to 8, characterized in that the reaction for the



hydroxycarbonylation of the lactones is carried out in the lactone itself as the liquid reaction medium.

10. Process according to one of Claims 1 to 8, characterized in that the reaction for the
- 5 hydroxycarbonylation of the lactones is carried out in a third solvent chosen from saturated or unsaturated aliphatic or aromatic carboxylic acids containing not more than 20 carbon atoms, saturated aliphatic or cycloaliphatic hydrocarbons and their chlorinated
- 10 derivatives which are liquid under the reaction conditions.
11. Process according to Claim 10, characterized in that the solvent represents from 10 % to 99 % by volume with respect to the total volume of the reaction
- 15 mixture, and preferably from 30 % to 90 % by volume.
12. Process according to one of Claims 1 to 11, characterized in that the water concentration in the reaction mixture is maintained at a value of
- 0.01 mol/litre to 3 mol/litre and preferably from
- 20 0.01 mol/litre to 2 mol/litre.