

The present invention relates to a process for the preparation of adipic acid by hydrocarboxylation of pentenic acids, that is to say by reacting water and carbon monoxide with at least one pentenic acid.

5 US Patent 3,579,551 has proposed a process for the preparation of carboxylic acids by reacting compounds containing ethylenic unsaturation with carbon monoxide and water, in the presence of a catalytic composition essentially comprising iridium compounds or complexes,
10 and an iodine-containing promoter. The compounds containing ethylenic unsaturation are selectively converted into carboxylic acids (linear and branched) by the reaction in question being performed, preferably in the liquid phase, at a temperature between 50 and 300°C
15 (preferably between 125 and 225°C), under partial pressures of carbon monoxide which are advantageously between 5 and 3,000 psia or even between 25 and 1000 psia.

 Any source of iridium appears able to be used and various sources of iodine-containing promoters are
20 mentioned: the I/Ir atomic ratio may vary within a wide range (1:1 to 2500:1) and preferably between 3:1 and 300:1.

 The liquid reaction medium may contain any solvent which is compatible with the catalytic system,
25 C₂-C₂₀ monocarboxylic acids being the preferred solvents.

 Example 1, which is performed starting with propylene, shows that such a system promotes the formation of branched carboxylic acids (isobutyric).

 Example 19, which is performed starting with
30 1-hexene, confirms the magnitude of the proportion of branched carboxylic acids thus obtained.

 This drawback (lack of selectivity for linear carboxylic acid) did not go unnoticed by the proprietor of the abovementioned US Patent. Indeed, in US Patent
35 No. 3,816,489, it is proposed to carry out the reaction in question with an I/Ir atomic ratio of between 3:1 and 100:1 in order to obtain predominantly terminal carboxylic acids.

 Although the principal advantage of such

techniques is not brought into question, in the case of starting materials chosen from nonfunctionalized compounds containing olefinic unsaturation and in particular in the case of the olefins themselves, the transposition of these techniques to starting materials which contain, besides the ethylenic unsaturation, a functional group which is reactive under the conditions of the reaction in question, comes up against numerous difficulties.

In particular, the first attempts at transpositions performed by the Applicant, starting with pentenic acids, resulted in an at least partial failure, reactions other than that specifically intended taking place to the detriment of, or even in total replacement for, this intended reaction, on account of the presence of a -COOH functional group on the starting material containing ethylenic unsaturation.

In Patent EP-A-0 493 273, relating to a process for the hydroxycarbonylation of pentenoic acids to adipic acid, in the presence of rhodium or a rhodium compound, an iodine-containing promoter and a cocatalyst chosen from the group consisting of iridium, ruthenium, osmium and compounds thereof, a control test (b) was performed with 3-pentenoic acid, using iridium trichloride as catalyst, hydrogen iodide as promoter and acetic acid as solvent, the I/Ir atomic ratio being 5.7. This test produced adipic acid in a very low yield of 1.2 %.

In such a context, it would clearly be desirable to have available a process which offers simultaneously good performance in the desired carbonylation reaction and appreciable selectivity for adipic acid.

The subject of the present invention is thus a process for the preparation of adipic acid by reacting water and carbon monoxide with at least one pentenic acid, in the presence of a catalyst based on iridium and at least one iodine-containing promoter, at an elevated temperature and at a pressure greater than atmospheric pressure, in at least one carboxylic acid chosen from saturated aliphatic carboxylic acids, ethylenic aliphatic

carboxylic acids and aromatic carboxylic acids, containing not more than 20 carbon atoms, the I/Ir atomic ratio being less than 10, and, when the catalyst is iridium trichloride and the solvent is acetic acid, the I/Ir atomic ratio then additionally being different from 5.7.

Within the context of the present invention, pentenoic acid means 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid and their mixtures.

4-Pentenoic acid leads to good results, but is still not readily available.

3-Pentenoic acid, taken alone or as a mixture with its isomers, is more particularly suitable on account of its accessibility and the satisfactory results which it produces within the context of the present process.

The process according to the present invention requires the presence of an iridium-based catalyst. Various sources of iridium are capable of being used.

By way of example of iridium sources which may be suitable for implementing the present process, there may be mentioned:

Ir metal; 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 ;
 $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
 $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
 $\text{Ir}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
 $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
 $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
 $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
 $\text{Ir}(\text{acac})(\text{CO})_2$
 $[\text{IrCl}(\text{Cod})]_2$
(Cod : 1,5-cyclooctadiene; acac: acetylacetonate)

The following are more particularly suitable for implementation of the present process: $[\text{IrCl}(\text{Cod})]_2$; $\text{Ir}_4(\text{CO})_{12}$ and $\text{Ir}(\text{acac})(\text{CO})_2$.

The quantity of iridium to be used may vary within a wide range.

In general, a quantity, expressed as moles of iridium metal per litre of reaction medium, of between 10^{-4} and 10^{-1} leads to satisfactory results. Smaller quantities may be used; it is observed, however, that the rate of reaction is low. Larger quantities have no drawbacks other than from an economic point of view.

The iridium concentration is preferably between 5×10^{-4} and 10^{-2} mol/l (inclusive).

Within the context of the present process, iodine-containing promoter means HI and organoiodine compounds capable of generating HI under the reaction conditions, and in particular C_1 - C_{10} alkyl iodides, methyl iodide being more particularly recommended.

According to an essential characteristic of the present process, the quantity of iodine-containing promoter to be used is such that the I/Ir molar ratio is less than 10. It turns out to be desirable for this ratio to be greater than or equal to 0.1. The I/Ir molar ratio is preferably between 1 and 5 (inclusive).

The presence of water is essential for performing the process according to the present invention. In general, the quantity of water to be used is such that the water/pentenic acid(s) molar ratio is between 0.01 and 10 (inclusive).

A larger quantity is not desirable on account of the loss of catalytic activity observed. The water/pentenic acid(s) molar ratio in the reaction medium may at any given moment be less than the minimum value indicated above, if, for example, the water is introduced continuously rather than being introduced with the other charges before the hydrocarboxylation reaction.

The water/pentenic acid(s) molar ratio is preferably between 0.01 and 1 (inclusive), the above comment relating to the minimum value being equally valid.

According to another of the essential characteristics of the present invention, the reaction is carried out in at least one carboxylic acid chosen from saturated aliphatic carboxylic acids, ethylenic aliphatic carboxylic acids and aromatic carboxylic acids, containing not

more than 20 carbon atoms.

The precise nature of the carboxylic acid is not critical within the context of the present process, provided that this acid is in the liquid state under the
5 reaction conditions.

By way of examples of carboxylic acids which may be suitable for implementation of the process according to the invention, there may be mentioned:

acetic acid, propionic acid, butyric acid,
10 valeric acid, adipic acid, 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid, mixtures of 2 or 3 of the above pentenic acids, benzoic acid and phenylacetic acid.

Use is preferably made of a C_2 - C_6 saturated aliphatic carboxylic acid. Acetic acid is more particularly
15 suitable for implementation of the present invention. Adipic acid, the preparation of which compound is the purpose of the process of the invention, is equally suitable.

Another preferred variant of the invention
20 consists in using 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid and the various mixtures of these acids, as carboxylic acids.

The quantity of carboxylic acid present in the reaction medium may vary within a wide range, for example
25 from 10 to 99 % (inclusive) of the volume of the reaction medium. This quantity is preferably between 30 and 99 % (inclusive) of the volume. When the carboxylic acid used is chosen from pentenic acids, the value is obviously situated within the upper region of the values indicated
30 above.

As indicated at the start of the present specification, the reaction is performed at a pressure greater than atmospheric pressure and in the presence of carbon monoxide.

35 Substantially pure or technical-grade carbon monoxide may be used, as is found on the market.

The reaction is preferably performed in the liquid phase, it being possible for the total pressure to vary within a wide range, and the reaction temperature

generally being between 100 and 240°C and preferably between 160 and 190°C.

The partial pressure of carbon monoxide is generally between 2 and 250 bar and, for good implementation of the process according to the invention, it will be between 5 and 100 bar.

The reaction medium contains the saturated aliphatic carboxylic acid, the ethylenic aliphatic carboxylic acid or the aromatic carboxylic acid, water, one or more sources of iridium, one or more iodine-containing promoters and, where appropriate, all or some of the pentenic acid or acids employed and of the reaction products.

At the end of the reaction or of the time allotted thereto, the adipic acid is separated out by any suitable means, for example by crystallization and/or distillation of the carboxylic acid.

The examples which follow illustrate the present invention.

EXAMPLE 1:

The following are introduced into a glass bulb flushed beforehand with argon:

33.6 mg (0.1 mmol) of iridium in the form of $[\text{IrCl}(\text{Cod})]_2$

0.045 g (0.2 mmol) of HI in the form of an aqueous 57% solution (by weight)

0.5 g (28 mmol) of water

2.0 g (20 mmol) of 3-pentenoic acid

10cm³ of acetic acid.

The bulb is placed in a 125-ml autoclave.

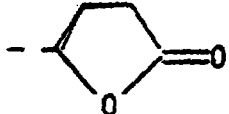
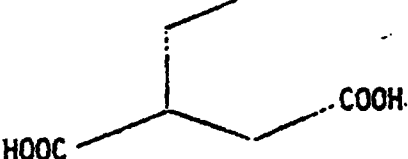
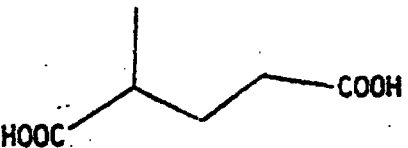
The autoclave is closed hermetically, placed in an oven incorporating agitation and connected to the pressurized gas supply. While cold, 2 bar of CO are introduced and the system is heated to 175°C over 20 minutes. When this temperature is reached, the pressure is adjusted to 20 bar.

After a reaction period of 20 minutes, the agitation and the heating are stopped; the autoclave is

then cooled and degassed.

The reaction solution is analysed by gas chromatography and by high performance liquid chromatography.

The amounts of products formed (molar yield relative to the 3-pentenoic acid converted) are as follows:

valeric acid	(Pa):		=	3.5 %
4-pentenoic acid	(P4):		=	1 %
3-pentenoic acid	(P3):		=	30 %
10 2-pentenoic acid	(P2):		=	6.5 %
γ-valerolactone:			=	10 %
ethylsuccinic acid (A3):			=	3.5 %
methylglutaric acid (A2):			=	16.5 %
adipic acid	(A1):		=	59 %

- 15 The degree of linearity (L) is 75 %
The extent of conversion of the 3-pentenoic acid (EC) is 70 %.

EXAMPLES 2 and 3:

A first series of tests is performed according to the experimental procedure described for Example 1, modifying only the quantity of HI charged.

- 5 The specific conditions and the results obtained, all conditions being otherwise equal, are presented in Table (I) below, in which the terms used are the same as for Example 1:

TABLE I

Ref.	HI/Ir	EC %	Al %	L %	M4L %
2	1	36	49	65	10
1	2	70	59	75	10
3	3	50	58	70	20

EXAMPLE 4

Example 3 is repeated according to the experimental procedure described for Example 1, decreasing the quantity of iridium in the form of $[\text{IrCl}(\text{Cod})]_2$: 12.6 mg (0.0375 mmol), the quantities of the various other charges remaining the same.

The HI/Ir molar ratio is thus 8.

The duration of the reaction at the reaction temperature is 60 minutes.

The results obtained are indicated below (with the terms used for Example 1):

- EC of 3-pentenoic acid: 58 %
- Al: 5 %
- L: 62 %
- M4L: 92 %

EXAMPLES 5 TO 12:

A series of tests is performed, in an autoclave and according to the experimental procedure which are described above, on a charge containing:

- 0.1 mmol of iridium in the form of $\text{Ir}_4(\text{CO})_{12}$
- 0.2 mmol of HI in the form of an aqueous 57% solution weight)
- 20 mmol of 3-pentenoic acid
- a variable quantity of water
- 10 cm³ of acetic acid.

The specific conditions and the results obtained after reaction for 20 minutes at a temperature of 175°C are presented in Table II below, in which $P(\text{CO})$ represents the partial pressure of carbon monoxide at the reaction temperature.

TABLE II

Ref.	H2O mmol	P(CO) bar	EC %	Al %	L %	M4L %
5	17	20	60	62.5	78	10
6	29	"	70	65.5	81	8.5
7	67	"	37	41	72	24
8	193	"	34	40	67	20
9	29	5	51	21	72	6.5
10	"	10	82	63	84	10
11	"	15	68	63	81	10.5
12	"	50	57	59	78	10

EXAMPLE 13:

Example 6 above is repeated, with only the temperature being modified (190°C).

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

EC (%) = 84

Al (%) = 39

L (%) = 76

M4L(%) = 9

EXAMPLE 14:

Example 6 above is repeated, with only the quantity of iridium charged being modified (0.05 mmol).

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

EC (%) = 26

Al (%) = 39

L (%) = 63

M4L(%) = 23

EXAMPLE 15:

Example 6 above is repeated, with the quantity of iridium charged being doubled.

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

EC (%) = 73

Al (%) = 56

L (%) = 82

M4L(%) = 9

CONTROL TEST:

5 Example 6 above is repeated, with HI being replaced by an equivalent quantity of HBr.

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

EC (%) = 9

10 Al (%) = 0

M4L(%) = 83

EXAMPLES 16 AND 17:

Example 6 above is repeated, with only the nature of the pentenoic acid charged being changed.

15 The specific conditions and the results obtained, all conditions being otherwise equal, are presented in Table III below:

TABLE III

Ref.	Acid charged	EC %	Al %	L %	M4L %	PA
20 6	3-pentenoic	70	65.5	81	8.5	3.5
16	4-pentenoic	100	63	88	14.5	3
17	2-pentenoic	45	54.5	88	6	24

EXAMPLE 18:

25 The following are introduced into a glass bulb which has been flushed beforehand with argon:

33.6 mg (0.1 mmol) of iridium in the form of [IrCl(Cod)]₂

0.045 g (0.2 mmol) of HI in the form of an aqueous 57% solution (by weight)

30 0.5 g (28 mmol) of water

11.9 g (119 mmol) of 3-pentenoic acid.

The bulb is placed in a 125-ml autoclave.

35 The autoclave is closed hermetically, placed in an oven incorporating agitation and connected to the pressurized gas supply. While cold, 2 bar of CO are introduced and the system is heated to 175°C over

20 minutes. When this temperature is reached, the pressure is adjusted to 20 bar.

After a reaction period of 55 minutes, the agitation and the heating are stopped and the reaction solution is analysed as in Example 1.

The following results are obtained (with the terms used for Example 1):

	- EC of 3-pentenoic acid:	34 %
	- Al:	71 %
10	- L:	86 %
	- M4L:	11 %

EXAMPLE 19:

Example 18 is repeated with the following charges:

15 33.6 mg (0.1 mmol) of iridium in the form of
 [$\text{IrCl}(\text{Cod})$]₂
 0.045 g (0.2 mmol) of HI in the form of an aque-
 ous 57% solution (by weight)
 0.5 g (28 mmol) of water
20 2.0 g (2 mmol) of 3-pentenoic acid
 10 g of adipic acid.

The following results are obtained (with the terms used for Example 1):

	- EC of 3-pentenoic acid:	95 %
25	- Al (adipic acid formed, excluding the acid charged at the start):	77 %
	- L:	86 %
	- M4L:	12 %

30 EXAMPLE 20:

Example 18 is repeated with the following charges:

 33.6 mg (0.1 mmol) of iridium in the form of
 [$\text{IrCl}(\text{Cod})$]₂
35 0.045 g (0.2 mmol) of HI in the form of an aque-
 ous 57% solution (by weight)
 0.5 g (28 mmol) of water
 2.0 g (2 mmol) of 3-pentenoic acid
 10 g of 2-pentenoic acid.

The following results are obtained (with the terms used for Example 1):

- EC of 3-pentenoic acid:	40 %
- Al:	59 %
- L:	83 %
- M4L:	3 %



CLAIMS

1. Process for the preparation of adipic acid by reacting water and carbon monoxide with at least one pentenic acid, in the presence of a catalyst based on iridium and at least one iodine-containing promoter, at an elevated temperature and at a pressure greater than atmospheric pressure, in at least one carboxylic acid chosen from saturated aliphatic carboxylic acids, ethylenic aliphatic carboxylic acids and aromatic carboxylic acids, containing not more than 20 carbon atoms, the I/Ir atomic ratio being less than 10, and, when the catalyst is iridium trichloride and the solvent is acetic acid, the I/Ir atomic ratio then additionally being different from 5.7.
2. Process according to claim 1, characterized in that the pentenic acid is chosen from 3-pentenoic acid, 2-pentenoic acid, 4-pentenoic acid and their mixtures.
3. Process according to either of claims 1 and 2, characterized in that the water/pentenic acid(s) molar ratio is less than or equal to 10.
4. Process according to one of claims 1 to 3, characterized in that the carboxylic acid is chosen from saturated C₂-C₆ aliphatic acids.
5. Process according to claim 4, characterized in that the carboxylic acid is acetic acid or adipic acid.
6. Process according to one of claims 1 to 3, characterized in that the carboxylic acid is chosen from 3-pentenoic acid, 2-pentenoic acid, 4-pentenoic acid and the mixtures of two or three of these.
7. Process according to one of claims 1 to 6, characterized in that the carboxylic acid represents at least 10 % of the volume of the reaction medium.
8. Process according to one of claims 4 to 6, characterized in that the carboxylic acid represents from 10 to 99 % (inclusive) and preferably from 30 to 99 % (inclusive) of the volume of the reaction medium.
9. Process according to one of claims 1 to 8, characterized in that the iridium concentration in the reaction medium is between 10⁻⁴ and 10⁻¹ mol/l (inclusive).



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10. Process according to one of claims 1 to 9, characterized in that the reaction temperature is between 100 and 240°C and preferably between 160 and 190°C.

5 11. Process according to one of claims 1 to 10, characterized in that the partial pressure of carbon monoxide is between 2 and 250 bar and preferably between 5 and 100 bar.

10 12. Process according to one of claims 1 to 11, characterized in that the I/Ir atomic ratio is greater than or equal to 0.1.

13. Process according to one of claims 1 to 12, characterized in that the I/Ir atomic ratio is between 1 and 5 (inclusive).