

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

5 A process was proposed, in American Patent 3,579,551, for the preparation of carboxylic acids by reaction of compounds containing ethylenic unsaturation with carbon monoxide and water in the presence of a catalytic composition, essentially comprising compounds
10 or complexes of iridium, and an iodinated promoter. The compounds containing ethylenic unsaturation are selectively converted into carboxylic acids (linear and branched) by the reaction in question carried out, preferably in liquid phase, at a temperature of between
15 50 and 300°C (preferably between 125 and 225°C), under carbon monoxide partial pressures advantageously of between 5 and 3,000 psia or, more specifically, between 25 and 1,000 psia.

 Any source of iridium appears to be able to be
20 used and various sources of iodinated promoters are mentioned; the I/Ir atomic ratio can vary within wide limits (1:1 to 2,500:1) and preferably between 3:1 and 300:1.

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

 Example 1, carried out starting with propylene, shows that such a system favours the formation of branched carboxylic acids (isobutyric).

30 Example 19, carried out starting with 1-hexene, confirms the extent of the proportion of branched carboxylic acids thus obtained.

 This disadvantage (lack of selectivity towards linear carboxylic acid) did not escape the attention of
35 the proprietor of the abovementioned American patent. Indeed, in American Patent No. 3,816,489, it is proposed to use the reaction in question with an I/Ir atomic ratio of between 3:1 and 100:1 in order predominantly to obtain terminal carboxylic acids.

Although the main interest of such techniques is not in question, in the case of starting materials chosen from the non-functionalized compounds containing olefinic unsaturation and, in particular, in the case of olefins themselves, many difficulties are encountered in extrapolating these techniques to starting materials which contain, in addition to the ethylenic unsaturation, a functional group which is reactive under the conditions of the reaction in question.

In particular, the first attempts at extrapolation carried out by the Applicant using pentenic acids as starting materials ended in an at least partial failure, reactions different from that specifically targeted being produced to the detriment, indeed with the total replacement, of the latter due to the presence of a -COOH functional group on the starting material containing ethylenic unsaturation.

In such a context, it would obviously be desirable to be able to have available a process which simultaneously offers good results in the targeted carbonylation reaction and an appreciable selectivity for adipic acid.

The subject of the present invention is thus a process for the preparation of adipic acid by reaction of water and carbon monoxide with at least one pentenic acid, in the presence of an iridium-based catalyst and of at least one iodinated promoter, at a high temperature, at a pressure greater than atmospheric pressure, in at least one solvent chosen from the group comprising saturated aliphatic or cycloaliphatic hydrocarbons and their halogenated derivatives, aromatic hydrocarbons and their halogenated derivatives and aliphatic, aromatic or mixed ethers, the I/Ir atomic ratio being less than 20.

Pentenic acid is understood to mean, within the scope of the present invention, penten-2-oic acid, penten-3-oic acid or penten-4-oic acid and their mixtures.

Penten-4-oic acid leads to good results but is not readily available.

Penten-3-oic acid, taken in isolation or as a mixture with its isomers, is more particularly suitable, considering its accessibility and the satisfactory results which it gives within the scope 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.

As examples of sources of iridium capable of being suitable for use in the present process, 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 ;

$\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;

$\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;

$\text{Ir}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;

$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;

$\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;

$\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;

$\text{Ir}(\text{acac})(\text{CO})_2$

$[\text{IrCl}(\text{Cod})]_2$

(Cod: 1,5-cyclooctadiene; acac: acetylacetonate).

More particularly suitable for use in 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 can vary within wide limits.

In general, a quantity, expressed in mole of metallic iridium per litre of reaction mixture, of between 10^{-3} and 10^{-1} leads to satisfactory results. Lower quantities can be used; however, the reaction velocity is observed to be low. Higher quantities have disadvantages only at an economic level.

Preferably, the concentration of iridium is between 5×10^{-3} and 10^{-1} (inclusive) mol/l.

Iodinated promoter is understood to mean, within the scope of the present process, HI and the organoiodine compounds capable of generating HI under the reaction

conditions and, in particular, the C₁-C₁₀ alkyl iodides. Preferably, HI is employed.

According to an essential characteristic of the present process, the quantity of iodinated promoter to be used is such that the I/Ir molar ratio is less than 20. It proves to be desirable for this ratio to be greater than or equal to 0.1. Preferably, the I/Ir molar ratio is less than 10. For a good implementation of the invention, it will be between 1 and 5 (inclusive).

The presence of water is vital to the running of 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 1 and 10 (inclusive).

A lower quantity has the disadvantage of limiting the conversion. A higher quantity is not desirable due to the loss of catalytic activity observed.

According to another of the essential characteristics of the present invention, the reaction is carried out in at least one solvent chosen from the group comprising the saturated aliphatic or cycloaliphatic hydrocarbons and their halogenated derivatives, the aromatic hydrocarbons and their halogenated derivatives and the aliphatic, aromatic or mixed ethers.

The precise nature of the solvent chosen from the abovementioned group is not critical within the scope of the present process, provided that the latter is in the liquid state under the reaction conditions.

As examples of such solvents, there may be mentioned: benzene, toluene, chlorobenzene, methylene chloride, 1,2-dichloroethane, hexane, cyclohexane and diphenyl ether.

The quantity of solvent present in the reaction mixture can vary within wide limits, for example from 10 to 99 % (inclusive) by volume of the reaction mixture. Preferably, this quantity is between 30 and 90 % by volume (inclusive).

As mentioned at the beginning of the present statement, the reaction is carried out under a pressure

greater than atmospheric pressure and in the presence of carbon monoxide.

5 It is possible to use carbon monoxide which is substantially pure or of technical quality, such as is commercially available.

The reaction is preferably carried out in the liquid phase, it being possible for the total pressure to vary within wide limits, and the reaction temperature being generally between 100 and 240°C and preferably
10 between 160 and 190°C.

The carbon monoxide partial pressure is generally between 1 and 250 bar and for a good implementation of the process according to the invention, it will be between 2 and 100 bar.

15 The reaction mixture contains at least one solvent chosen from the group defined above, water, one or more sources of iridium, one or more iodinated promoters and, if need be, all or part of the pentenic acid(s) involved and the products of the reaction.

20 At the end of the reaction or of the time allotted to the latter, adipic acid is separated by any suitable means, for example by crystallization and filtration.

The examples below illustrate the present
25 invention.

EXAMPLE 1:

The following are introduced into a glass flask purged beforehand with argon:

30 30 mg (0.1 mmol) of iridium in the form of $\text{Ir}_4(\text{CO})_{12}$
30 0.045 g (0.2 mmol) of HI in the form of a solution in chlorobenzene (1 ml)
0.54 g (30 mmol) of water
35 2 g (20 mmol) of penten-3-oic acid
9 cm³ of chlorobenzene.

The flask is placed in a 125 ml autoclave.

The autoclave is hermetically closed, placed in an oven equipped with agitation and connected to a supply

of pressurized gas. 2 bar of CO are admitted while cold and the mixture is heated to 175°C over 20 minutes. When this temperature is reached, the pressure is adjusted to 20 bar.

5 After a period of reaction of 30 minutes, the agitation and the heating are halted; the autoclave is then cooled and degassed.

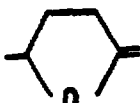
The reaction solution is analysed by gas phase chromatography and by high performance liquid
10 chromatography.

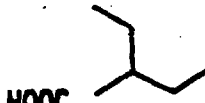
The quantities of products formed (molar yield in relation to penten-3-oic acid charged) are as follows:

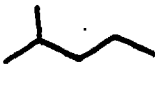
valeric acid (Pa):  COOH = 5 %

penten-2-oic acid (P2):  COOH = 5 %

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γ-valerolactone (M4L):  O = 6 %

ethylsuccinic acid (A3):  COOH = 2 %

methylglutaric acid (A2):  COOH = 11 %

adipic acid (A1): HOOC  COOH = 71 %

The degree of linearity (L) is 84 %.

20 The degree of conversion of penten-3-oic acid (DC) is 93 %.

EXAMPLE 2:

Example 1 above is repeated except that HI is introduced in the form of a solution (0.2 mmol) in acetic
25 acid (1 ml).

All conditions being otherwise the same, substantially the same results are obtained except that the presence of penten-2-oic acid is no longer detected and that the molar yield of γ -valerolactone in relation to penten-3-oic acid charged (M4L) is 12.5 %.

EXAMPLES 3 to 6; Comparative test (a):

Example 1 above is repeated using solvents of a different type and using a solution of HI (0.2 mmol) in acetic acid. The particular conditions as well as the results obtained are collated in Table I below in which - t denotes the duration of the test at temperature.

TABLE I

Ref.	Solvent (type)	t min	DC %	A1 %	L %	M4L %
2	Chlorobenzene	30	93	71	84	12.5
3 (*)	Methylene chloride	35	100	70	84	10.0
4	Toluene	35	95	75	84	7.5
5	Cyclohexane	30	96	68	80	8
6	Diphenyl ether	40	100	63	78	12
a	water/toluene (50/50 vol.)	120	18	ε	ND	40

(*) In this Example, the total pressure at temperature is 30 bar.

ND: not determined

In the reference test (a), the formation of a predominant quantity of pentanoic acid is recorded [PA (%) = 40].

EXAMPLES 7 to 8; Comparative test (b):

According to the procedure described for

Example 1, a series of tests is carried out in toluene and by modifying the quantity of HI charged.

5 The particular conditions as well as the results obtained, all conditions being otherwise the same, are collated in Table (II) below, in which the conventions used are the same as for Example 1 and t denotes the duration of the test at temperature:

TABLE II

Ref.	HI/Ir	t min	DC %	A1 %	L %	M4L %
a	0	90	0	-	-	-
1	2	30	93	71	84	6
7	5	35	99	44	78	33
8	9	85	78	21	81	64

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* C L M S *

CLAIMS

1. Process for the preparation of adipic acid by reaction of water and carbon monoxide with at least one pentenic acid, in the presence of an iridium-based catalyst and of at least one iodinated promoter, at a high temperature, at a pressure greater than atmospheric pressure, in at least one solvent chosen from the group comprising saturated aliphatic or cycloaliphatic hydrocarbons and their halogenated derivatives, aromatic hydrocarbons and their halogenated derivatives and aliphatic, aromatic or mixed ethers, the I/Ir atomic ratio being less than 20.
2. Process according to claim 1, characterized in that the pentenic acid is chosen from penten-3-oic acid, penten-2-oic acid, penten-4-oic acid and their mixtures.
3. Process according to either of the preceding claims, characterized in that the water/pentenic acid(s) molar ratio is less than or equal to 10.
4. Process according to any one of the preceding claims, characterized in that the solvent is chosen from benzene, toluene, chlorobenzene, hexane, cyclohexane, methylene chloride, 1,2-dichloroethane and diphenyl ether.
5. Process according to any one of the preceding claims, characterized in that the solvent represents at least 10 % of the volume of the reaction mixture.
6. Process according to claim 5, characterized in that the solvent represents from 30 to 90 % (inclusive) of the volume of the reaction mixture.
7. Process according to any one of the preceding claims, characterized in that the concentration of iridium in the reaction mixture is between 10^{-3} and 10^{-1} mol/l (inclusive).
8. Process according to any one of the preceding claims, characterized in that the reaction temperature is between 100 and 240°C and preferably between 160 and 190°C.
9. Process according to any one of the preceding claims, characterized in that the carbon monoxide partial



pressure is between 1 and 250 bar and preferably between 2 and 100 bar.

10. Process according to any one of the preceding claims, characterized in that the I/Ir atomic ratio is
5 less than 10.

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

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

13. Process according to any one of the preceding claims, characterized in that HI is used as iodinated promoter.