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PROCESS FOR THE ISOMERIZATION OF CARBOXYLIC ACIDS

The present invention relates to a process for the isomerization of carboxylic acids, more precisely of saturated, branched carboxylic acids, to give corresponding linear acids.

The hydroxycarbonylation of pentenoic acids to prepare adipic acid always leads to the formation of larger or smaller quantities of branched diacids, as by-products of the reaction.

Exploiting these branched diacids therefore represents, in particular, a major problem to be solved, within the context of an industrial process for the preparation of adipic acid by hydroxycarbonylation of pentenoic acids.

Patent EP-A-0,374,687 describes a process for the isomerization of saturated carboxylic acids, by heating under a pressure of carbon monoxide, in the presence of a rhodium catalyst and of an iodine-containing or bromine-containing promoter.

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

More specifically, it consists of a process for the isomerization, by heating, of at least one saturated, branched carboxylic acid, characterized in that the process is carried out in the presence of an effective quantity of an iridium catalyst and of an

iodine-containing or bromine-containing promoter, the promoter/Ir molar ratio being between 0.1/1 and 20/1.

Among saturated branched carboxylic acids, the branched diacids are the most advantageous ones to exploit from an economic point of view, on account of the large quantities formed during the hydroxycarbonylation of pentenoic acids for the preparation of adipic acid.

More precisely, the acids in question are 2-methylglutaric acid, 2-ethylsuccinic acid and their mixtures with one another and/or with other carboxylic acids or lactones formed at the same time as these acids, such as for example adipic acid, the pentenoic acids, valeric acid and gamma-valerolactone.

In the above mixtures, the compounds other than 2-methylglutaric acid and 2-ethylsuccinic acid may represent up to 50% by weight of the total weight of the mixture.

Various sources of iridium are capable of being used in order to obtain the iridium catalyst necessary in the present process.

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

- Ir metal; IrO_2 ; Ir_2O_3 ;
- $IrCl_3$; $IrCl_3.3H_2O$;
- $IrBr_3$; $IrBr_3.3H_2O$;
- IrI_3 ;
- $Ir_2(CO)_4Cl_2$; $Ir_2(CO)_4I_2$;

- $Ir_2(CO)_8$; $Ir_4(CO)_{12}$;
- $Ir(CO)[P(C_6H_5)_3]_2I$;
- $Ir(CO)[P(C_6H_5)_3]_2Cl$;
- $Ir[P(C_6H_5)_3]_3I$;
- $HIr[P(C_6H_5)_3]_3(CO)$;
- $Ir(acac)(CO)_2$;
- $[IrCl(cod)]_2$;

(acac = acetylacetonate ; cod = 1,5-cyclooctadiene).

The iridium catalysts which are most particularly suitable are: $[IrCl(cod)]_2$, $Ir_4(CO)_{12}$ and $Ir(acac)(CO)_2$.

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 10^{-1} leads to satisfactory results. Smaller quantities may be used, but it is observed, however, that the reaction rate is slow. Larger quantities have no disadvantages other than from the economic viewpoint.

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

Iodine-containing or bromine-containing 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.

The reaction is carried out in the liquid phase. The operating temperature is generally from 120°C to 300°C, and preferably from 150°C to 250°C.

Although the isomerization according to the process of the invention may be carried out in the absence of carbon monoxide, it is preferable to operate in its presence.

The total pressure at the reaction temperature can thus 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 may be substantially pure carbon monoxide or technical grade carbon monoxide, such as are found commercially.

The isomerization reaction of the saturated branched carboxylic acids is carried out either in the acid itself as liquid reaction medium, or in a dissolving intemediary.

As dissolving intermediary, it is possible, in particular, to use saturated or unsaturated

aliphatic or aromatic carboxylic acids containing not more than 20 carbon atoms, in so far as they are liquid under the reaction conditions. By way of examples of such carboxylic acids, there may be mentioned acetic acid, propionic acid, butanoic acid, valeric acid, adipic acid, the pentenoic acids, benzoic acid and phenylacetic acid.

Other classes of solvents may also be used, especially saturated aliphatic or cycloaliphatic hydrocarbons and their chlorinated derivatives, in so far as they are liquid under the reaction conditions. By way of 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.

Water is very often present in the reaction mixture. Generally, it represents from 0 to 20% by weight of the reaction mixture, and preferably from 0 to 10%.

When the isomerization reaction is carried out in a solvent, an advantageous variant consists in operating in a water/water-miscible solvent mixture, such as for example water/acetic acid. On such an

assumption, the values for the proportions of the water/water-miscible solvent mixture in the reaction mixture are those which have been mentioned above for the solvent alone.

The isomerization process according to the invention makes it possible to exploit, in particular, the saturated branched carboxylic diacids which are obtained in greater or lesser quantities during the hydroxycarbonylation of pentenoic acids. This enables an increase to be obtained in the overall yield of a process for the preparation of adipic acid from butadiene via the 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 standard methods used in chemistry, in order to separate the various compounds formed and the unreacted saturated branched acids, it being possible for the latter to be subjected to a repeat isomerization.

The process according to the invention may be implemented in continuous or discontinuous fashion. When it is carried out in continuous fashion, the relative ratios of the reactants, catalyst, promoter and solvent can be fixed at an optimum value by a person skilled in the art, whereas, generally, in a process which is implemented in discontinuous fashion, these various ratios change in accordance with the

progressive conversion of the reactants.

The examples which follow illustrate the invention.

EXAMPLE 1.

Into a 125 cm^3 autoclave purged beforehand with argon, the following are successively introduced:

- $[IrCl(cod)]_2$: 0.84 mmol
- hydrogen iodide (in aqueous solution at a concentration of 57% by weight): 1.2 mmol
- 2-methylglutaric acid : 39 mmol
- acetic acid : 40 cm^3

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 and the system is then heated to 230°C. The pressure is adjusted at this temperature to 25 bar using CO (which corresponds to a partial pressure of CO of 17 bar measured at 25°C) and this pressure is maintained for 5 hours at 230°C.

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

The following results are obtained:

- degree of conversion (DC) of 2-methylglutaric acid : 18 %
- molar yield (RY) of adipic acid relative

to the methylglutaric acid converted : 37 %

- RY of 2-ethylsuccinic acid : 6 %
- RY of gamma-valerolactone : 6 %
- RY of 3-pentenoic acid : 10 %
- RY of 2-methylbutanoic acid : 26 %
- RY of valeric acid : 16 %

EXAMPLE 2.

Example 1 is repeated under the same conditions and with the same quantities of the same reactants, but using 2.5 mmol of hydrogen iodide and 0.42 mmol of $[IrCl(cod)]_2$.

The following results are obtained:

DC of 2-methylglutaric acid : 36 %

RY of adipic acid : 28 %

EXAMPLE 3.

Example 1 is repeated under the same conditions and with the same quantities of the same reactants, but using 2.5 mmol of hydrogen iodide and operating at 200°C.

The following results are obtained:

DC of 2-methylglutaric acid : 13 %

RY of adipic acid : 30 %

EXAMPLE 4.

Example 3 is repeated under the same conditions and with the same quantities of the same reactants, but without connecting the autoclave to the carbon monoxide supply.

The following results are obtained:

DC of 2-methylglutaric acid : 60 %

RY of adipic acid : 11 %

It is noted that a very large quantity of monoacids containing 5 carbon atoms (especially valeric and methylbutanoic acids) is obtained.

EXAMPLE 5.

Into a 50 cm^3 glass ampoule, purged beforehand with argon, the following are successively introduced :

- $[IrCl(cod)]_2$: 0.21 mmol
- hydrogen iodide (in aqueous solution at a concentration of 57% by weight): 0.54 mmol
- 2-methylglutaric acid : 78 mmol

The glass ampoule is placed in a 125 cm^3 autoclave, purged beforehand with argon. 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 230°C. The pressure is adjusted at this temperature to 100 bar with the aid of CO (which corresponds to a partial pressure of CO of 59 bar measured at 25°C) and this pressure is maintained for 2 hours at 230°C.

The autoclave is next cooled and then degassed, and the reaction mixture is analysed by GC and HPLC.

The following results are obtained:

DC of 2-methylglutaric acid : 20 %

RY of adipic acid : 37 %

EXAMPLE 6.

Example 5 is repeated under the same conditions and with the same quantities of the same reactants, but operating at a CO pressure of 25 bar at 230°C instead of 100 bar.

The following results are obtained :

DC of 2-methylglutaric acid : 39 %

RY of adipic acid : 35 %

EXAMPLE 7.

Example 5 is repeated under the same conditions and with the same quantities of the same reactants, but operating at a CO pressure of 25 bar at 230°C instead of 100 bar and allowing reaction to proceed for 30 min at this temperature instead of 2 h.

The following results are obtained :

DC of 2-methylglutaric acid : 9 %

RY of adipic acid : 52 %

EXAMPLE 8.

Example 5 is repeated under the same conditions and with the same quantities of the same reagents, but operating at a CO pressure of 10 bar at 230°C instead of 100 bar.

The following results are obtained :

DC of 2-methylglutaric acid : 62 %

RY of adipic acid : 20 %

EXAMPLE 9.

Example 5 is repeated under the same conditions and with the same quantities of the same

reagents, but operating at a temperature of 200°C instead of 230°C.

The following results are obtained :

DC of 2-methylglutaric acid : 3 %

RY of adipic acid : 64 %

EXAMPLE 10.

Example 6 is repeated under the same conditions and with the same quantities of the same reactants, but operating at a temperature of 200°C instead of 230°C.

The following results are obtained :

DC of 2-methylglutaric acid : 5 %

RY of adipic acid : 73 %

EXAMPLE 11.

Example 8 is repeated under the same conditions and with the same quantities of the same reagents, but operating at a temperature of 200°C instead of 230°C.

The following results are obtained :

DC of 2-methylglutaric acid : 6 %

RY of adipic acid : 83 %

EXAMPLE 12.

Example 6 is repeated under the same conditions and with the same quantities of the same reagents, but additionally charging 7.25 mmol of water initially.

The following results are obtained :

DC of 2-methylglutaric acid : 15 %

RY of adipic acid : 41 %

EXAMPLE 13.

Example 5 is repeated under the same conditions and with the same quantities of the same reactants, but replacing HI with 0.54 mmol of HBr at a concentration of 47% by weight in water.

The following results are obtained :

DC of 2-methylglutaric acid : 7 %

RY of adipic acid : 53 %

EXAMPLE 14.

Example 6 is repeated under the same conditions and with the same quantities of the same reactants, but replacing HI with 0.54 mmol of HBr at a concentration of 47% by weight in water.

The following results are obtained :

DC of 2-methylglutaric acid : 17 %

RY of adipic acid : 25 %

EXAMPLE 15.

Example 8 is repeated under the same conditions and with the same quantities of the same reactants, but replacing HI with 0.54 mmol of HBr at a concentration of 47% by weight in water.

The following results are obtained :

DC of 2-methylglutaric acid : 24 %

RY of adipic acid : 18 %

EXAMPLE 16.

Into a 50 cm^3 glass ampoule purged beforehand with argon, the following are successively introduced :

- $[IrCl(cod)]_2$: 0.21 mmol
- hydrogen iodide (in aqueous solution at a concentration of 57 % by weight) : 0.30 mmol
- 2-ethylsuccinic acid : 10 mmol
- acetic acid : 10 cm^3

The process is carried out as in Example 5, with a CO pressure at the operating temperature of 25 bar and maintaining the test at 230°C for 5 hours.

The following results are obtained :

DC of 2-ethylsuccinic acid : 26 %

RY of adipic acid : 47 %

RY of 2-methylglutaric acid : 19 %

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CLAIMS

1. Process for the isomerization, by heating, of at least one saturated, branched carboxylic acid, characterized in that the process is carried out in the presence of an effective quantity of an iridium catalyst and of an iodine-containing or bromine-containing promoter, the promoter/Ir molar ratio being between 0.1/1 and 20/1.

2. Process according to claim 1, characterized in that the saturated, branched carboxylic acid used is chosen from 2-methylglutaric acid, 2-ethylsuccinic acid and their mixtures with one another and/or with other carboxylic acids or lactones formed at the same time as these acids, such as adipic acid, the pentenoic acids, valeric acid and gamma-valerolactone.

3. Process according to claim 2, characterized in that, in the mixture used, the compounds other than 2-methylglutaric acid and 2-methylsuccinic acid represent up to 50% by weight of the total weight of the mixture.

4. Process according to one of claims 1 to 3, characterized in that the iridium catalyst used is chosen from :

- Ir metal; IrO_2 ; Ir_2O_3 ;
- $IrCl_3$; $IrCl_3.3H_2O$;
- $IrBr_3$; $IrBr_3.3H_2O$;
- IrI_3 ;

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- $Ir_2(CO)_4Cl_2$; $Ir_2(CO)_4I_2$;
- $Ir_2(CO)_8$; $Ir_4(CO)_{12}$;
- $Ir(CO)[P(C_6H_5)_3]_2I$;
- $Ir(CO)[P(C_6H_5)_3]_2Cl$;
- $Ir[P(C_6H_5)_3]_3I$;
- $HIr[P(C_6H_5)_3]_3(CO)$;
- $Ir(acac)(CO)_2$;
- $[IrCl(cod)]_2$.

5. Process according to one of claims 1 to 4, characterized in that the quantity of catalyst, 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 10^{-2} mol/litre.

6. Process according to one of claims 1 to 5, characterized in that the iodine-containing or bromine-containing 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 conditions.

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

8. Process according to one of claims 1 to 7, characterized in that the reaction is carried out in the presence of carbon monoxide, at a partial pressure of carbon monoxide, measured at 25°C, of 0.5 bar to 100 bar, and preferably from 1 bar to 80 bar.

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9. Process according to one of claims 1 to 8, characterized in that the reaction is carried out in the liquid phase at a temperature of 100°C to 300°C, and preferably from 150°C to 250°C.

10. Process according to one of claims 1 to 9, characterized in that the isomerization reaction of the carboxylic acid is carried out in the carboxylic acid itself as liquid reaction medium.

11. Process according to one of claims 1 to 9, characterized in that the isomerization reaction of the saturated branched carboxylic acid is carried out in a dissolving intermediary 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 derivatives which are liquid under the reaction conditions.

12. Process according to claim 11, 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.

13. Process according to one of claims 1 to 12, characterized in that the reaction is carried out in the presence of water.

14. Process according to one of claims 1 to 13, characterized in that the water represents from 0 to 20% by weight of the reaction mixture, and

preferably from 0 to 10%.

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