

CAPROLACTAM PREPARATION

The present invention relates to the aminomethylation of pentenoic acid derivatives, by reaction with carbon monoxide, hydrogen and ammonia, in
5 order to prepare caprolactam.

Caprolactam is the constituent of Nylon 6.

Numerous access routes to caprolactam exist, in particular from butadiene.

In particular, the successive preparation of
10 a pentenenitrile by hydrocyanation of butadiene and then of a 5-cyanovaleric acid derivative, the carbonyl functional group being introduced by virtue of a carbonylation reaction or a hydroformylation reaction, and finally the conversion of the nitrile functional
15 group to an amine functional group by a hydrogenation reaction, in order to obtain caprolactam and/or aminocaproic acid, has been envisaged. This process suffers from a large number of stages and requires the successive use of hydrocyanic acid and then of carbon
20 monoxide, which can be harmful to the economic advantage of such a process.

In the process of the invention, caprolactam is obtained directly in a single stage from a pentenoic acid derivative, which is much simpler than the
25 processes already envisaged from butadiene.

The pentenoic acid derivatives are, for example, esters. Such esters can for their part be readily obtained from butadiene according to well-

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described processes.

The metals which can catalyse this type of reaction are, for example, cobalt, palladium, rhodium or iridium.

5 The reaction employed here, which consists in converting a C=C compound to a CH-CH-CH₂-N product, has the name of aminomethylation. The aminomethylation of olefins is a known reaction catalysed by a variety of metals from group VIII; however, it is generally
10 limited to the synthesis of secondary or tertiary amines, because the amine formed by aminomethylation is a better nucleophile than the starting amine. Thus, in the case of the use of ammonia, the reactivity of the product formed by aminomethylation of the olefin with
15 ammonia reacts faster with another olefin than ammonia.

We have found that this limitation could be circumvented by using the intramolecular cyclization of the amine to a lactam. By way of example, this aim is achieved by using a pentenoic acid ester as substrate.

20 More specifically, the invention consists of a process for the preparation of caprolactam, characterized in that the aminomethylation of pentenoic acid derivatives is carried out, by reaction with carbon monoxide, hydrogen and ammonia, at a temperature
25 greater than 30°C and in the presence of a catalyst based on at least one metal from group VIII of the Periodic Classification of the Elements.

The pentenoic acids to which the invention

relates are the various isomers of this compound, namely cis-pent-2-enoic, trans-pent-2-enoic, cis-pent-3-enoic, trans-pent-3-enoic and pent-4-enoic acids.

The derivatives of the pentenoic acids in the context of the invention are the compounds where the OH group of the acidic functional group has been replaced by a potentially better nucleofuge group, such as O-R or S-R, in which R represents an alkyl, cycloalkyl, aralkyl, aryl or silyl residue. More particularly, the derivatives used are the esters of alcohols comprising from 1 to 6 carbon atoms.

Use may be made of any mixture of derivatives of the various pentenoic isomers. However, use will preferably be made of mixtures where the derivatives of the pent-3-enoic acids predominate. The mixture of pentenoic acid derivatives can additionally comprise a minor amount of 4-methylbutyrolactone and of derivatives of other carboxylic acids comprising 5 carbon atoms, such as valeric acid, at a content preferably of less than 20% by weight and more preferably still of less than 10% by weight.

The concentration by weight of the pentenoic acid derivatives can vary within wide limits, depending on whether the reaction is carried out in the presence of a solvent or not and depending on the degree of progression of the reaction. By way of indication, it is, for example, between 5 and 99% by weight.

The reaction is advantageously carried out in

the presence of a solvent. The amount of solvent employed varies between 10 and 95% by weight of the reaction mixture.

This solvent can be highly varied in nature.

5 The choice may in particular be made of alcohols, aliphatic ethers, aromatic ethers, mixed ethers, nitriles, acyclic amides, cyclic amides, aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, chlorinated cycloaliphatic
10 hydrocarbons or the mixtures of several of these solvents.

In the case where an alcohol is used as solvent or as part of a mixture of solvents and where the aminomethylation of a pentenoic acid ester is being
15 carried out, the alcohol corresponding to the said ester is preferably used.

As non-limiting examples, the solvents which can be used are ethanol, methanol, isopropanol, diphenyl ether, isopropyl ether, acetonitrile,
20 dimethylformamide, N-methylpyrrolidone, benzene, toluene, xylenes, chlorobenzenes, dichloromethane, dichloroethanes, hexane and cyclohexane.

In the context of an industrial implementation of the process, recycling operations
25 carried out on the catalyst and on the unreacted pentenoic acid derivatives can result in the introduction into the reaction mixture of more or less significant amounts of other compounds and in

particular of caprolactam product. In the context of the invention, these compounds will be regarded as forming an integral part of the solvent system.

The catalyst is based on at least one metal from group VIII. Use may be made, as source of such catalysts, of the metallic elements or various organometallic complexes or salts, such as chlorides, iodides, bromides, metal carbonyls, or carboxylates, these being mentioned as non-limiting examples.

The catalyst is preferably based on at least one of the metals taken from rhodium, iridium, ruthenium, iron or cobalt. The catalyst is optionally used in combination with promoters, such as phosphorus derivatives and/or $Q^{n+}X_n$ salts, where n represents 1 or 2, Q representing an alkali metal element (n=1) or an alkaline earth metal element (n=2) and X a halogen.

Preferably, Q is chosen from lithium, sodium, potassium, magnesium and calcium and X is chosen from fluorine, chlorine, bromine and iodine.

The phosphorus derivatives are of the $R^1R^2R^3P$ type, where R^1 , R^2 and R^3 are the same or different and represent an alkyl or aralkyl or cycloalkyl residue comprising from 1 to 20 carbon atoms which can additionally comprise one or more atoms taken from nitrogen, oxygen, sulphur, phosphorus and iron and which can form one or more rings with one another. The following are suitable as non-limiting illustrative examples of such promoters: triphenylphosphine,

tricyclohexylphosphine, phosphanorbornadienes,
phosphanorbornenes, phosphanorbornanes,
1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenyl-
phosphinomethyl)cyclobutane, 1,3-bis(diphenyl-
5 phosphino)propane, 1,4-bis(diphenylphosphino)butane or
1,1'-bis(diphenylphosphino)ferrocene.

The amount of catalyst to be employed can
vary within wide limits. In general, an amount,
expressed as total number of moles of metals used as
10 catalysts per litre of reaction mixture, of between 10^{-5}
and 10^{-1} leads to satisfactory results. Lower amounts
can be used but it is observed, however, that the
reaction rate is low. Higher amounts are only
disadvantageous from an economic viewpoint. This amount
15 is preferably between 10^{-4} and 5×10^{-2} mol per litre of
reaction mixture.

The aminomethylation reaction can be carried
out at a temperature generally between 60°C and 230°C
and preferably between 80°C and 200°C .

20 The carbon monoxide partial pressure,
measured at 25°C , is between 0.5 and 300 bar. It is
preferably between 2 and 200 bar and more preferably
still between 5 and 150 bar.

The hydrogen partial pressure, measured at
25 25°C , is between 0.5 and 200 bar. It is preferably
between 1 and 150 bar and more preferably still between
2 and 100 bar.

The hydrogen/carbon monoxide molar ratio is

between 10/1 and 1/10, preferably between 5/1 and 1/2.

The amount of ammonia involved can vary within wide limits. However, it is preferable to use an excess with respect to the substrate. The
5 ammonia/substrate molar ratio is between 1/1 and 100/1 and preferably between 1.1/1 and 50/1.

The process of the invention can be implemented continuously or batchwise. There will therefore be grounds for adjusting the various
10 operating conditions defined above according to the implementation chosen.

The example which follows illustrates the invention.

88.6 mg of $\text{Rh}_6(\text{CO})_{16}$, 1.11 g of methyl
15 pentenoate and 20 ml of methanol are successively introduced into a 125 ml Hastelloy® B2 autoclave; the autoclave is closed and 4.58 g of NH_3 are introduced via an isolation chamber. The autoclave is then pressurized with 40 bar of CO and 80 bar of hydrogen at 20°C.
20 Agitation by shaking is begun and the temperature of the autoclave is brought to 150°C; the total pressure is then 163 bar. After 195 min, the pressure in the autoclave has decreased by 2 bar; heating is then halted. After cooling, the autoclave is degassed and
25 then opened; the khaki-green reaction mass is analysed by Gas Chromatography (GC). The caprolactam yield of 33% is confirmed by coupled GC/MS (mass spectrometry).

CLAIMS

1. Process for the preparation of caprolactam, characterized in that the aminomethylation of pentenoic acid derivatives is carried out, by
5 reaction with carbon monoxide, hydrogen and ammonia, at a temperature greater than 30°C and in the presence of a catalyst based on at least one metal from group VIII of the Periodic Classification of the Elements.
2. Process according to claim 1,
10 characterized in that the reaction is carried out in the presence of a solvent.
3. Process according to either one of claims 1 and 2, characterized in that the total amount of catalyst is between 10^{-5} and 10^{-1} mol per litre of
15 reaction mixture and preferably between 10^{-4} and 5×10^{-1} mol per litre of reaction mixture.
4. Process according to any one of claims 1 to 3, characterized in that the temperature is between 60°C and 230°C and preferably between 80°C and 200°C.
- 20 5. Process according to any one of claims 1 to 4, characterized in that the catalyst is based on at least one of the metals taken from rhodium, iridium, ruthenium, iron or cobalt.
6. Process according to any one of claims 1
25 to 5, characterized in that the ammonia/substrate molar ratio is between 1/1 and 100/1 and preferably between 1.1/1 and 50/1.
7. Process according to any one of claims 1

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to 6, characterized in that the carbon monoxide partial pressure, measured at 25°C, is between 0.5 and 300 bar, preferably between 2 and 200 bar and more preferably still between 5 and 150 bar.

5 8. Process according to any one of claims 1 to 7, characterized in that the hydrogen partial pressure, measured at 25°C, is between 0.5 and 200 bar, preferably between 2 and 150 bar and more preferably still between 5 and 100 bar.

10 9. Process according to any one of claims 1 to 8, characterized in that the hydrogen/carbon monoxide molar ratio is between 10/1 and 1/10, preferably between 5/1 and 1/2.

15 10. Process according to any one of claims 1 to 9, characterized in that the pentenoic acid derivative is an ester, preferably a methyl or ethyl ester.

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