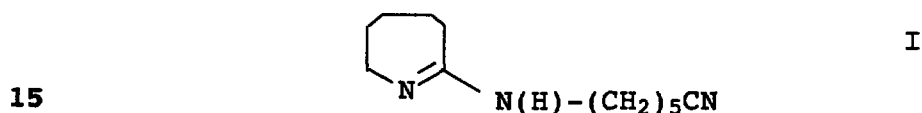


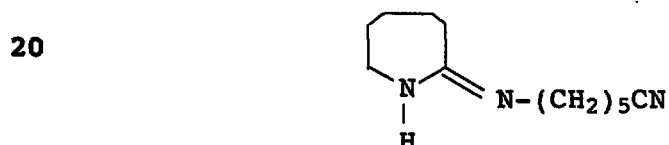
Preparation of caprolactam

The present invention relates to an improved process for
5 preparing caprolactam by reacting 6-aminocapronitrile with water
in the presence of catalysts.

On heating or storage at room temperature, 6-aminocapronitrile
forms a brown tetrahydroazepine derivative (THA derivative I) of
10 the formula



THA derivative I shall also encompass its tautomeric form



EP-A-497,333 describes the direct polymerization of
25 polycaprolactam starting from 6-aminocapronitrile. The problem to
be solved in the process mentioned was the removal of
tetrahydroazepine ("THA") before the polymerization step, since
tetrahydroazepine leads to discoloration of the polymer obtained
on polymerizing caprolactam in the presence of tetrahydroazepine.
30 EP-A-497,333 proposes solving the problem by means of a treatment
with a basic compound such as an alkali metal hydroxide or an
alkali metal alkoxide. Following the treatment,
6-aminocapronitrile can be conveniently separated from the
reaction mixture by distillation, which is not possible without
35 such a treatment.

EP-A 502,439 solves the problem of removing THA in the presence
of 6-aminocapronitrile by treatment with sodium borohydride. Here
too 6-aminocapronitrile can be readily separated from the
40 reaction mixture by distillation after the treatment.

DE-B-25 42 396 and DE-B-25 42 397 describe the conversion of
gamma-aminobutyronitrile into a mixture comprising
2-(N-gamma-cyanopropyl)amino-delta¹-pyrroline ("CAP") and
45 2-amino-delta¹-pyrroline ("AP"), and also the further hydrolysis
of the isolated CAP to 2-pyrrolidone in the absence of catalysts.
Neither reference indicates whether the corresponding THA



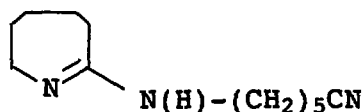
derivative I can be converted into caprolactam in a similar manner in liquid phase in the presence of heterogeneous catalysts. Furthermore, in the cited DE references CAP is first isolated as a pure substance before it is hydrolyzed. It might
5 therefore be expected that the use of mixtures comprising THA derivative I would promote the formation of undesirable by-products. It is also known that five-membered rings are easier to form than seven-membered rings (see Römpp Chemie Lexikon, 9th edition, editors Falbe and Regitz, Georg Thieme Verlag, New
10 York). Altogether and on the basis of experience with THA it might therefore be expected that THA derivative I would lead to discolored caprolactam in the cyclization of 6-aminocapronitrile and to discolored polycaprolactam in the direct conversion of 6-aminocapronitrile into polycaprolactam, unless separated off
15 before the cyclization and before the polymerization step.

It might further be expected that THA derivative I would reduce the lifetime of the catalyst used in the polymerization, since it was known from US 5,162,567 that heating THA produces high
20 boilers, ie. compounds or mixtures with a higher boiling point than 6-aminocapronitrile (accordingly making it easy to remove the 6-aminocapronitrile). High boilers, however, tend to form polymeric or oligomeric decomposition products which can form deposits on catalyst surfaces and so reduce not only the lifetime
25 but also the activity of the catalysts.

It is an object of the present invention to provide a process for cyclizing 6-aminocapronitrile to caprolactam wherein THA derivative I reduces neither the lifetime nor the activity of the
30 cyclization catalyst, nor leads to a caprolactam-containing reaction mixture whose UV number is equal to or higher than that prior to the cyclization step. Preferably the post-cyclization UV number should be smaller than pre-cyclization as a function of the pre-cyclization THA derivative I content. Furthermore, any
35 THA derivative I present in the reaction mixture for the direct polymerization of 6-aminocapronitrile shall be easy to remove or it shall be possible to conduct the reaction in such a way that THA derivative I is eliminated.

40 We have found that this object is achieved by a process for preparing caprolactam by reacting 6-aminocapronitrile with water in the presence of catalysts, which comprises using a starting mixture of 6-aminocapronitrile and the tetrahydroazepine derivative of the formula





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and conducting the reaction in liquid phase in the presence of a heterogeneous catalyst.

The present invention also provides tetrahydroazepine derivative
10 I, a process for its preparation, and the use of THA derivative I for preparing caprolactam.

The reaction of the present invention is carried out in liquid phase in the presence of heterogeneous catalysts at temperatures
15 from generally 140 to 320°C, preferably from 160 to 280°C; the pressure is generally within the range from 1 to 250 bar, preferably from 5 to 150 bar, care having to be taken to ensure that, under the conditions employed, the reaction mixture is predominantly (ie. without the catalyst, which is present in
20 solid phase) liquid. The residence times are generally within the range from 1 to 120, preferably from 1 to 90, in particular from 1 to 60, min. In some cases residence times from 1 to 10 min will prove completely adequate.

25 The amount of water used is generally at least 0.01 mol, preferably from 0.1 to 20 mol, in particular from 1 to 5 mol, per mole of THA derivative I.

Advantageously THA derivative I is used in the form of a from 1
30 to 50% strength by weight, in particular from 5 to 50% strength by weight, particularly preferably from 5 to 30% strength by weight, solution in water (in which case the solvent is then also the reactant) or in water-solvent mixtures. Examples of suitable solvents are alkanols such as methanol, ethanol, n- and
35 i-propanol, n-, i- and t-butanol and polyols such as diethylene glycol and tetraethylene glycol, hydrocarbons such as petroleum ether, benzene, toluene, xylene, lactams such as pyrrolidone or caprolactam or alkyl-substituted lactams such as N-methylpyrrolidone, N-methylcaprolactam or N-ethylcaprolactam
40 and also carboxylic esters, preferably of carboxylic acids having from 1 to 8 carbon atoms. Ammonia too can be present in the reaction. It is of course also possible to use mixtures of organic solvents. Mixtures of water and alkanols in a water:alkanol weight ratio of 1-75:25-99, preferably 1-50:50-99,
45 have been determined to be particularly advantageous in some cases.



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The THA derivative I content in the 6-aminocapronitrile of the starting mixture can be within the range from 0.01 to 95% by weight, in particular from 0.1 to 50% by weight, particularly preferably from 0.5 to 20% by weight.

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The starting mixture customarily has, depending on the level of THA derivative I, a UV number (sum of all absorbances of a 10% by weight solution in ethanol at wavelengths from 280 to 400 nm, based on a pathlength of 5 cm) within the range from 5 to 40,000.

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The starting mixture is obtainable by heating 6-aminocapronitrile with or without solvent. From experience to date, the temperature can be within the range from 20 to 280°C, in particular within the range from 50 to 250°C, particularly preferably within the range

- 15 from 100 to 230°C. The reaction times are customarily within the range from 10 minutes to 20 hours. As expected, shorter reaction times are possible at higher temperatures. The reaction can be carried out at pressures within the range from 100 kPa to 25 MPa, preferably from 500 kPa to 20 MPa. It can further be advantageous
- 20 to carry out the reaction in the presence of acidic homogeneous or heterogeneous catalysts such as mineral acid, carboxylic acids, sulfonic acids, titanium dioxide, aluminum oxide, acid ion exchangers or Lewis acids.

- 25 If desired, pure THA derivative I can be obtained for example by distillation of unconverted 6-aminocapronitrile, solvents and any by-products.

- Examples of suitable heterogeneous catalysts include: acidic,
- 30 basic or amphoteric oxides of the elements of the second, third or fourth main group of the periodic table, such as calcium oxide, magnesium oxide, boron oxide, aluminum oxide, tin oxide or silicon dioxide as pyrogenic silica, as silica gel, diatomaceous earth, quartz or mixtures thereof, also oxides of metals of
- 35 secondary groups two to six of the periodic table, such as titanium oxide, amorphous, as anatase and/or rutile, zirconium oxide, zinc oxide, manganese oxide or mixtures thereof. It is also possible to use oxides of the lanthanides and actinides, such as cerium oxide, thorium oxide, praseodymium oxide, samarium
- 40 oxide, rare earth mixed oxide, or mixtures thereof with the aforementioned oxides. Further catalysts can be, for example:

- vanadium oxide, niobium oxide, iron oxide, chromium oxide, molybdenum oxide, tungsten oxide or mixtures thereof. Mixtures
- 45 between the oxides mentioned are also possible. It is also possible to use sulfides, selenides and tellurides such as zinc

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telluride, tin selenide, molybdenum sulfide, tungsten sulfide, sulfides of nickel, of zinc and of chromium.

The aforementioned compounds may be doped, ie. contain, compounds 5 of main groups 1 and 7 of the periodic table.

Also suitable are zeolites, phosphates and heteropolyacids and also acidic and alkali iron exchangers such as, for example, Naphion®.

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If desired, these catalysts may contain up to 50% by weight each of copper, tin, zinc, manganese, iron, cobalt, nickel, ruthenium, palladium, platinum, silver or rhodium.

- 15 The catalysts can be used as solid catalyst or supported catalyst, depending on the composition of the catalyst. For instance, titanium dioxide can be used in the form of a titanium dioxide extrudate or in the form of a thin layer applied to a carrier. Any method described in the literature is suitable for
20 applying TiO_2 to a carrier such as silicon dioxide, aluminum oxide or zirconium dioxide. For instance, a thin layer of TiO_2 can be applied by hydrolysis of organotitaniums such as titanium isopropoxide or titanium butoxide, or by hydrolysis of TiCl_4 or other inorganic Ti-containing compounds. Sols which contain
25 titanium dioxide are also suitable.

Particular preference is given to catalysts which contain no constituents that are soluble under the conditions of the reaction.

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- In a further preferred embodiment, the reaction is carried out in a fixed bed reactor. A fixed bed process is customarily carried out with tablets or extrudates having diameters within the range from 1 to 10 mm. In principle, however, the reaction can also be
35 carried out in suspension.

- In a further preferred embodiment, the reaction is carried out in particular in the presence of a heterogeneous catalyst based on titanium dioxide, zirconium dioxide, cerium oxide or aluminum
40 oxide.

- Aluminum oxide is generally suitable in all modifications obtained by heating the precursor compounds aluminum hydroxide (gibbsite, boehmite, pseudoboehmite, bayerite and diaspore) at
45 different temperatures. These include in particular gamma- and alpha-alumina and mixtures thereof.



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The oxides can be used in pure form (purity of the respective oxide > 80% by weight), as a mixture of the abovementioned oxides, in which case the sum of the abovementioned oxides should be > 80% by weight, or as supported catalyst, in which case the
5 abovementioned oxides can be applied to a mechanically and chemically stable carrier usually with a high surface area.

The pure oxides can be prepared by precipitation from aqueous solutions, for example titanium dioxide by the sulfate process or
10 by other processes such as the pyrogenic production of fine alumina, titania or zirconia powders which are commercially available.

Mixtures of various oxides can be prepared in various ways. The
15 oxides or their precursor compounds, which are convertible into the oxides by calcination, can be prepared for example by coprecipitation from solution. This generally brings about very good dispersion of the two oxides used. The oxide or precursor mixtures can also be precipitated by precipitating one oxide or
20 precursor in the presence of a fine suspension of the second oxide or precursor. A further method consists in mechanically mixing the oxide or precursor powders, this mixture can be used as a starting material for producing extrudates or tablets.

25 Supported catalysts can be prepared by customary methods. For instance, the oxides can be applied to the support by simply impregnating the support with their sols. The sol volatiles are customarily removed from the catalyst by drying and calcining. Sols of this type are commercially available for titania, alumina
30 and zirconia.

A further way of applying layers of the active oxides is the hydrolysis or pyrolysis of organic or inorganic compounds. For instance, a ceramic support can be coated with a thin layer of
35 titanium dioxide by hydrolysis of titanium isopropoxide or other titanium alkoxides. Other suitable compounds include TiCl_4 , zirconyl chloride, aluminum nitrate and cerium nitrate. Suitable supports are powders, extrudates or tablets of the aforementioned oxides themselves or of other stable oxides such as silica. The
40 supports used can be macroporous to improve the mass transport.

In a further particularly preferred embodiment, the catalyst used is titanium dioxide with an anatase content within the range from 100 to 5, preferably from 99 to 10, % by weight and a rutile
45 content within the range from 0 to 95, preferably from 1 to 90, % by weight, based on the total amount of titanium dioxide.

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THA derivative I is preferably used for preparing caprolactam by heating it with water/solvent at a temperature within the range from 140 to 320°C, preferably within the range from 160 to 280°C, and a pressure within the range from 100 to 2500, in particular within the range from 500 to 2000, kPa in the presence of the abovementioned heterogeneous catalysts, preferably titania-containing, similarly to the abovementioned starting mixture, using a molar ratio of tetrahydroazepine derivative I to water within the range from 0.01:1 to 20:1, preferably from 0.5:1 to 20:1.

The abovementioned starting mixture as aqueous solution and THA derivative I alone can be directly converted into polycaprolactam by heating by known methods, for example described in EP-A-150,295.

The advantage of the process of the present invention is that it provides a convenient way of processing THA-derivative-I-containing reaction mixtures with 6-aminocapronitrile into caprolactam and, if desired, into polycaprolactam. The products and product mixtures thus obtained are free of troublesome THA derivative I. Thus there is no need for further process steps in the use of additional agents, compared with the removal of THA from corresponding reaction mixtures.

In certain circumstances it can even be advantageous to convert 6-aminocapronitrile in whole or in part into THA derivative I by preheating to temperatures from 20 to 280°C and to use the resulting mixture of THA derivative I and 6-aminocapronitrile for the cyclization over oxidic catalysts.

Examples

Example 1:

400 g of 6-aminocapronitrile (ACN) were heated to 200°C for 8 h. Distillation yielded as second fraction at 0.1 mbar and 140°C 40 g of THA derivative I (yield 10%) as a pure compound. The characterization was carried out by means of NMR spectroscopy:

¹H-NMR (250 MHz, DMSO-d₆, TMS, ppm):

4.2 (s, broad, 1 H), 3.2 (m, 2 H), 2.9 (t, 2H), 2.45 (t, 2H), 2.25 (m, 2H), 1.7 - 1.1 (m, 12 H).

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¹³C-NMR (62.9 MHz, DMSO-d₆, TMS, ppm):

163.3 s, 120.6 s, 47.0 t, 41.6 t, 32.9 t, 30.6 t,
29.7 t, 28.4 t, 26.0 t, 25.6 t, 24.8 t, 16.2 t.

5 Example 2:

A 10% by weight ethanolic solution of THA derivative I was pumped together with 2 mol of water (corresponding to 3.2% by weight of the total solution) through a titania-packed tubular reactor
10 (diameter 6 mm; length 800 ml [sic]) at 70 ml/h. The reactor temperature was 230°C, the pressure was 80 bar. The hourly output was a 9.7% ethanolic caprolactam solution. The solution further obtained [sic] 0.8% by weight of recyclable ethyl 6-aminocaproate and also 0.2% by weight of recyclable 6-aminocapronitrile. The
15 caprolactam yield was 80%, the selectivity including the recyclable compounds was 95%.

Example 3:

20 A 10% by weight ethanolic solution consisting of 95% by weight of ACN and 5% by weight of THA derivative I was pumped together with 2 mol of water (corresponding to 3.2% by weight of the total solution) through a titania-packed tubular reactor (diameter 6 mm; length 800 ml [sic]) at 70 ml/h. The reactor temperature
25 was 230°C, the pressure was 80 bar. The hourly output was a 9.1% ethanolic caprolactam solution. The solution further contained 0.4% by weight of recyclable ethyl 6-aminocaproate and also 0.1% by weight of recyclable 6-aminocapronitrile. The caprolactam yield was 91%, the selectivity including the recyclable compounds
30 was 95%.

Example 4:

A 10% by weight ethanolic solution consisting of 99% by weight of
35 ACN and 1% by weight of THA derivative I was pumped together with 2 mol of water (corresponding to 3.2% by weight of the total solution) through a titania-packed tubular reactor (diameter 6 mm; length 800 ml [sic]) at 70 ml/h. The reactor temperature was 230°C, the pressure was 80 bar. The hourly output was a 9.0%
40 ethanolic caprolactam solution. The solution further contained 0.4% by weight of recyclable ethyl 6-aminocaproate and also 0.1% by weight of recyclable 6-aminocapronitrile. The caprolactam yield was 90%, the selectivity including the recyclable compounds was 95%.

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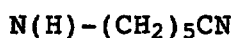
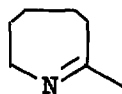


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We claim:

1. A process for preparing caprolactam by reacting
5 6-aminocapronitrile with water in the presence of catalysts,
which comprises using a starting mixture of
6-aminocapronitrile and the tetrahydroazepine derivative of
the formula

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- 15 and conducting the reaction in liquid phase in the presence
of a heterogeneous catalyst.
2. A process as claimed in claim 1, wherein the heterogeneous
catalyst contains no constituents that are soluble under the
20 conditions of the reaction.
3. A process as claimed in claim 1 or 2, wherein the reaction is
carried out in a fixed bed reactor.
- 25 4. A process as claimed in any of claims 1 to 3, wherein the
reaction is carried out in the presence of a heterogeneous
catalyst based on titanium dioxide, zirconium dioxide, cerium
oxide or aluminum oxide.
- 30 5. A process as claimed in any of claims 1 to 4, wherein the
catalyst used comprises titanium dioxide having an anatase
content within the range from 5 to 100% by weight and a
rutile content within the range from 0 to 95% by weight,
based on the total amount of titanium dioxide.
- 35 6. A process as claimed in any of claims 1 to 5, wherein the
starting mixture has a UV number (sum of all absorbances of a
10% by weight solution in ethanol at wavelengths from 280 to
400 nm, based on a pathlength of 5 cm) within the range from
40 5 to 40,000.
7. The tetrahydroazepine derivative of the formula

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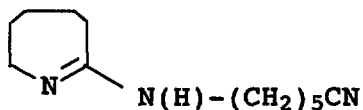
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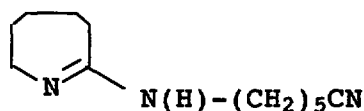


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8. A process for preparing the tetrahydroazepine derivative I of claim 7, which comprises heating 6-aminocapronitrile at from 100 to 300°C.
- 10 9. The use of tetrahydroazepine derivative I for preparing caprolactam and polycaprolactam.
10. A process for preparing caprolactam, which comprises reacting tetrahydroazepine derivative I with water at a temperature within the range from 140 to 320°C and a pressure within the range from 100 to 2500 kPa in a molar ratio of tetrahydroazepine derivative I to water within the range from 0.01:1 to 20:1.
- 20 11. A process for preparing polycaprolactam by heating an aqueous solution of 6-aminocapronitrile, which comprises including THA derivative I

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in the aqueous solution.

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